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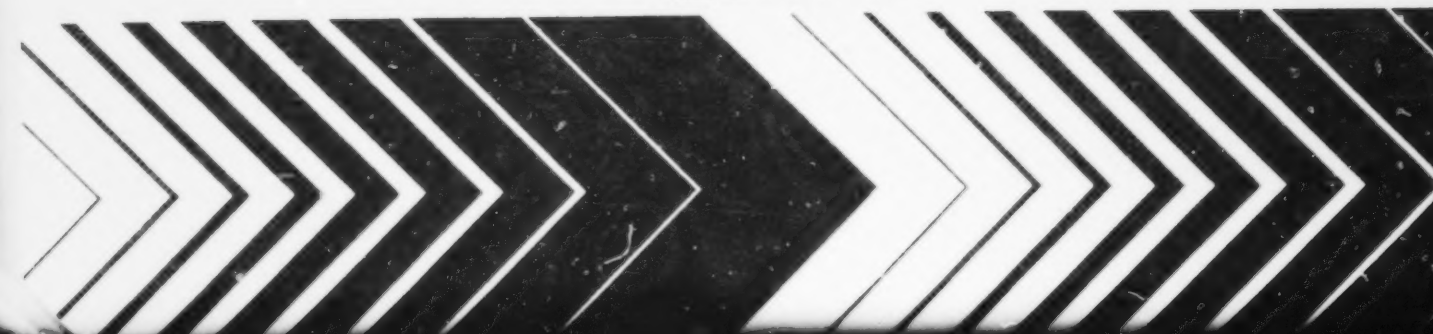
Research and Development



Remedial Action, Treatment, and Disposal of Hazardous Waste

Proceedings of the Sixteenth Annual RREL Hazardous Waste Research Symposium

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OF HAZARDOUS WASTE

Proceedings of the Sixteenth Annual Hazardous Waste Research Symposium
Cincinnati, Ohio, April 3-5, 1990

Sponsored by the U.S. EPA, Office of Research & Development
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Cincinnati, OH 45268

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FOREWORD

Today's rapidly developing technologies and industrial practices frequently carry with them the increased generation of materials, that if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs. These provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between researchers and users.

These Proceedings from the 1990 Symposium provide the results of projects recently completed by RREL and current information on projects presently underway. Those wishing additional information on these projects are urged to contact the author or the EPA Project Officer.

RREL sponsors a symposium each year in order to assure that the results of its research efforts are rapidly transmitted to the user community. The 1990 symposium attracted over 800 attendees from industry, Federal and State agencies, consulting firms, and universities. The 1991 symposium is planned for April 9, 10, and 11 in Cincinnati, Ohio.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The Sixteenth Annual Research Symposium on Remedial Action, Treatment, and Disposal of Hazardous Waste was held in Cincinnati, Ohio, April 3-5, 1990. The purpose of this Symposium was to present the latest significant research findings from ongoing and recently completed projects funded by the Risk Reduction Engineering Laboratory (RREL).

These Proceedings are organized in three sections: Sessions A and B consist of paper presentations. Session C contains the poster abstracts. Subjects include remedial action treatment and control technologies for waste disposal, landfill liner and cover systems, underground storage tanks, and demonstration and development of innovative/alternative treatment technologies for hazardous waste. Alternative technology subjects include thermal destruction of hazardous wastes, field evaluations, existing treatment options, emerging treatment processes, waste minimization, and biosystems for hazardous waste destruction.

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PIC Formation - Research Status and
Control Implications

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ABSTRACT

Control of emissions of toxic organic and organometallic compounds is one of the major technical and sociological issues surrounding the further implementation of incineration as a waste disposal alternative. In this paper, we briefly review the status of research concerning the emission of organic products of incomplete combustion (PICs). Emphasis is placed on the completeness of full-scale emissions test data and any identifiable deficiencies in our fundamental knowledge of PIC formation. From the laboratory perspective, the urgent need for detailed studies of PIC characterization, yields, and emission mechanisms at elevated temperatures is discussed. The benefits of interactions between laboratory-scale PIC studies, PIC toxicological studies, and sampling and analysis methods development for full-scale systems is also discussed.

INTRODUCTION

Of all the issues surrounding toxic waste disposal, the potential formation and emission of so-called "Products of Incomplete Combustion" (PICs) from the thermal disposal of toxic wastes is the most controversial. Much of the controversy is due to the lack of understanding of PICs, the current regulations only addressing destruction and removal efficiency of so-called "Principal Organic Hazardous Constituents" (POHCs) contained in the waste stream. This has led to the unfortunate public misconception of incineration as a "landfill in the sky."

It would seem that this important subject and controversy which has raged all through the 80's would be well researched and significant strides made towards answering key issues. However, we in reality know very little about PIC emissions. The purpose of this discussion is to define what we really know about PICs, what we think we know, and what we don't know. Although every effort has been made to approach this subject scientifically and arrive at logical, factually-based conclusions, there will undoubtedly continue to arise non-factual or even clearly incorrect statements concerning PICs. It is hoped that this paper will at least serve to establish a framework for rational discussion of the issues surrounding PICs.

WHAT WE KNOW

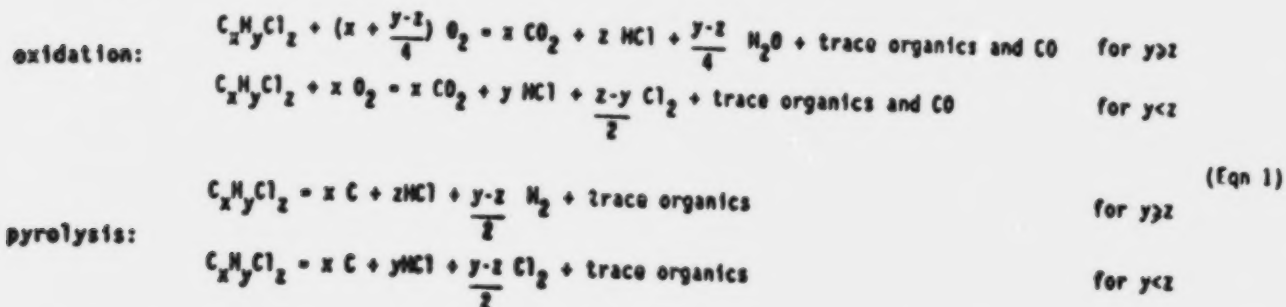
There are only a few issues for which we have sufficient data that agrees with scientific theory that will allow us to say we know this about PICs. Although we do not have enough data to advance a series of "Laws of PIC Formation," we can advance several theories. These theories are discussed below.

Theory 0 - PICs are a natural consequence of thermal degradation of toxic wastes

This theory is so fundamental and obvious that it is designated as the Zeroth Theory of PIC Formation. The formation of stable PICs has been repeatedly demonstrated in numerous lab and full-scale studies.¹ Possibly, one source of confusion is the concentration or toxicity a combustion byproduct must have to be designated a PIC.² From a scientific point of view any product of the oxidative or pyrolytic degradation of a compound, other than the thermodynamically most stable end-products, should be included in the definition of PIC. If we want to designate PICs of environmental concern where toxicity and concentration are factors, then we can define a new term; Toxic, Principal, Product of Incomplete Combustion (ToP-PIC). The question is not if PICs are emitted from hazardous waste incinerators, because they will undoubtedly be formed and emitted from any combustion source. The true issue is whether they are of environmental consequence, which is a very complex issue indeed.

Theory 1 - PIC emission rates are kinetically, not thermodynamically, controlled

If an incinerator achieves thermodynamic equilibrium, then one only needs to know the elemental composition of the waste/fuel/oxidizer (air) feed system and the temperature to calculate the emissions from the system. For example, thermodynamically complete combustion or pyrolysis of a chlorinated hydrocarbon at 1800°F results in the formation of a few stable products, e.g., CO₂, H₂O, HCl, H₂, Cl₂, etc., and trace quantities of carbon monoxide (CO) and organic byproducts (cf. Eqn. 1):



Numerous calculations of PIC emission rates have been performed assuming an incinerator at equilibrium. These calculations typically demonstrate that observed incinerator PIC concentrations are at least 10 orders of magnitude greater than predicted based on equilibrium.^{4,5} Chemical reaction kinetics undoubtedly plays a large role in PIC formation. However, physical kinetics, such as vaporization and waste/air mixing, can also contribute to kinetically limited routes of PIC formation.

Theory 2 - Deviation from normal, average operating conditions are responsible for most PIC emissions

Modern, well-designed and managed incinerators operate at temperatures in excess of 1800°F, residence times greater than 2.0 s, and at least 50% excess air. Detailed elementary and global oxidation kinetic models consistently show that destruction efficiencies (DE's) for POHCs under these conditions are greater than 99.9999% for even the most stable compounds. Similar calculations for PICs result in yields < 0.000001 (cf. columns 3, 4, and 6, Table 1).

Since the nominal operating range of incinerators preclude measurable POHC or PIC emissions, we are left with the conclusion that temporal or spatial excursions from the measured conditions are responsible for the observed emissions. These "failure modes" may be due to excursions in temperature (thermal), residence time (temporal), or oxygen concentration (mixing).

TABLE 1

Kinetic Calculations of the Destruction Efficiency for PICs¹
for Various Flame and Post-Flame Reaction Conditions

POHC	PIC	Optimal Flame DE ²	Optimal Thermal DE ³	Thermal Failure DE ⁴	Overall (Optimal) DE ⁵	Overall (Failure) DE ⁶
1,1-Dichloroethane	Chloroethene	99.9999+	99.9999+	99.9997	99.9999+	99.9999+
Pentachloroethane	Tetrachloroethene	99.9999+	99.9999+	27.0164	99.9999+	99.2702
Chlorobenzene	Benzene	99.9999+	99.9999+	92.2267	99.9999+	99.9223

Notes:

1. PIC destruction calculations based on analytical solution of the following reaction scheme (cf. reference 10 for kinetic parameters):



2. DE calculated for optimal flame conditions ($T_f = 2780^\circ\text{F}$, $t_f = 0.1$ s).
3. DE calculated for optimal post-flame conditions ($T_{pf} = 2300^\circ\text{F}$, $t_{pf} = 2.0$ s).
4. DE calculated for sub-optimal post-flame conditions ($T_{pf} = 1340^\circ\text{F}$, $t_{pf} = 2.0$ s).
5. Overall DE based on 99% destruction of the waste experiencing flame conditions and 1% of the waste bypassing the flame but experiencing optimal post-flame conditions.
6. Overall DE based on 99% destruction of the waste experiencing flame conditions and 1% of the waste experiencing failure post-flame conditions.

WHAT WE THINK WE KNOW

In addition to these theories which the preponderance of the data support, there is a body of qualitative and semi-quantitative lab and field data that have led to certain observations concerning PIC emissions. We refer to these as partially verified hypothesis.

Hypothesis 1 - Flame reactions control bulk or absolute emissions of PICs while post-flame (thermal) reactions control relative emission rates

This hypothesis is based on the reasonable assumption (Theory 2) that flame temperatures are high enough that any material experiencing nominal oxidizing flame conditions will be totally destroyed (POHCs and PICs) (cf., column 3, Table 1). The small fraction of the waste that somehow escapes the flame is responsible for observed POHC and PIC emissions. Since compounds fed as mixtures will now experience very similar post-flame destruction conditions, the relative thermal stability (oxidative or pyrolytic) of the escaping POHCs will determine their relative emission rates. In a similar manner, the post-flame propensity for formation and stability of PICs will control their relative emission rates (cf. column 7, Table 1).

However, there is insufficient data on the range of temperature, residence times, and oxygen concentrations that can potentially exist in an incinerator flame to absolutely state that no PICs are emitted from the flame. Although a two zone system seems to be conceptually useful, there is also a transition zone between the flame and post-flame zones where the distinction is blurred. In addition, differing vaporization rates of compounds can, in principle result in not all species experiencing the exact same combustion conditions. However, preliminary calculations suggest that droplet vaporization does not significantly affect relative DEs.

Hypothesis 2 - Most PIC emissions are the result of pyrolysis pathways

This is essentially a narrowing of the focus of the failure mode concept presented as the Second Theory of PIC Formation. Theoretical calculations concerning the oxidation of the most stable organic PICs indicate that temperatures below 1450°F for post-flame mean residence times of 2.0 s (cf. Columns 5 and 7, Table 1), or residence times less than 0.1 s for post-flame mean temperatures of 2300°F, are necessary for measurable PIC breakthrough. Since these temperatures are so low, it seems reasonable that pyrolysis pathways (which are much slower than oxidation reactions) may be responsible for a large fraction of POHC and PIC emissions.¹¹ This hypothesis has been partially supported by comparison of actual versus predicted CO emissions.¹² Since CO is only destroyed under oxidative conditions (primarily by OH), its stack concentration may be considered an indicator of the fraction of the incinerator which is acting as an oxidizer. Theoretical calculations indicate that CO levels should be on the order of a few ppb instead of the observed levels of 1 ppm - 100 ppm, suggesting a significant fraction of the CO does not experience an oxidative environment. Full-scale emissions of undestroyed POHCs also agree best with a theoretical prediction of POHC stability based on pyrolysis kinetics.¹³

Recent bench-scale experiments simulating the burning of plastics in a rotary kiln suggest that rapid thermal degradation results in a "transient puff" of hydrocarbons and chlorocarbons that can overload the system such that intimate waste/air mixing is not completed.¹⁴ Consequently, high concentrations of various PICs and soot are observed, apparently due to a transient pyrolysis condition.

Some researchers have argued that upset pyrolysis conditions in full-scale incineration facilities actually result in lower PIC emissions.² However, other researchers have shown that the high levels of soot that are formed may act as a reservoir for the PICs by surface adsorption.¹⁵ Although air emissions may be mitigated by a high efficiency particulate APCD, the total PIC yield and environmental burden is increased. The impact is simply shifted from the air to the land.

There also exists a measurable number of cases where emissions do not correlate with pyrolysis kinetics.¹³ In these instances, relative POHC and PIC emission rates may be due to other "physical" kinetic conditions which are facility specific.

Hypothesis 3 - A significant fraction of the observed PICs is formed outside the high temperature zones

A detailed study of the types of PICs emitted from full-scale hazardous waste incinerators, boilers, and kilns suggests that as high as 50% of observed PICs are likely formed by radical-radical and radical-O₂ association reactions (cf. Table 2). These types of reactions are important as the system temperature is lowered because high activation energy unimolecular and radical-molecule reactions are not favorable. This may explain why thermally fragile PICs such as chloroform, 1,1,1-trichloroethane, and carbon tetrachloride are observed in the effluent of full-scale systems.¹⁶ In addition, it has been proposed and limited full-scale data suggest that formation of polychlorinated dibenzo-p-dioxins (PCDDs) is due to surface catalyzed reactions in the cool zones of the incinerator (i.e., transfer ducts air pollution control devices).^{17,18} Both lab and full-scale research on the mechanism of PCDD formation is incomplete, and no quantitative study of gas-phase formation of PCDD from possible precursors has been performed.

Hypothesis 4 - A significant fraction of observed PICs is due to fuel/waste interactions

Analysis of full-scale data reveals that many of the observed PIC emissions are aromatic and polynuclear aromatic (PNAs) species, i.e., benzene, toluene, naphthalene, etc. These compounds are commonly observed in the effluent from most combustion devices. However, further analysis indicates that the presence of chlorine containing wastes increases the emission of these species as well as partially chlorinated hydrocarbons.¹⁹ Although chlorination of a stable hydrocarbon is kinetically unfavorable, already chlorinated radicals may participate in condensation-type molecular growth reactions resulting in formation of chlorinated aromatic species and PNAs. Chlorine can also increase overall PIC emissions through the traditionally proposed effect of flame inhibition.²⁰

However, not enough parametric full-scale studies have been performed to confirm the hypothesis. Although preliminary lab studies support this concept, the chemistry of chlorinated hydrocarbons and other hazardous materials is only beginning to be addressed.

Hypothesis 5 - Carbon monoxide and total unburned hydrocarbons are surrogates for PIC emissions

From a scientific viewpoint, the emission rate of a surrogate should correlate (viz. have a statistically significant relationship through a continuous function) with the emission rate of a specific PIC or total PICs. From a regulatory viewpoint, it appears that a reasonable surrogate must only have a concentration greater than the PIC of interest such that if the CO concentration is below a given level, then the PIC will be below a given environmentally acceptable level.²¹

The concept of CO as a PIC surrogate arises from the fact that CO is more stable than any organic PIC. Total unburned hydrocarbons (TUHC) has been

TABLE 2

Prevalent, High-Yield PICs^{a,b} and their Postulated Formation Mechanisms
from Full-Scale Incinerators, Boilers, and Kilns

Compound	Geometric Mean ^c Emission Rate ($\mu\text{g}/\text{min}$)	Formation Mechanism
Benzene	38,950 ^d 10,047 ^e 6,757 ^f	Radical- molecule
Chloroform	31,391 ^e 2,250 ^f 1,234 ^d	Association
Methylene Chloride	96,408 ^e 2,100 ^d 1,623 ^f	Radical- molecule
Toluene	21,053 ^e 1,982 ^f	Radical- molecule
Tetrachloroethylene	96,408 ^e	Radical- molecule
Carbon Tetrachloride	10,308 ^e	Association
Chloromethane	9,593 ^e	Radical- molecule
1,1,1-Trichloroethane	8,628 ^e	Association
1,2-Dichloroethane	2,977 ^e	Association
Naphthalene	1,461 ^f	Radical- molecule

Footnotes:

^a Prevalent PICs defined as PICs observed in at least 75% of all tests; this excludes tests at sites where PICs were designated as a POHC in the waste feed.

^b High-yield PICs defined as PICs with geometric mean emission rates $\geq 1000 \mu\text{g}/\text{min}$ for the incinerator and kiln tests and PICs with geometric emission mean rates $\geq 7500 \mu\text{g}/\text{min}$ for the boiler tests.

^c PIC emission rate calculated as the geometric mean for all sites; geometric mean of data for individual runs based on the number of measurements above quoted detection limits.

^d PIC emission rate measured in kiln tests.

^e PIC emission rate measured in boiler tests.

^f PIC emission rate measured in incinerator tests.

proposed as a PIC surrogate because TUHC, in principal, is the total of un-destroyed POHC and organic PICs. Results of some full-scale tests indicate that CO and TUHC meet the regulatory definition of a surrogate for some PICs at some facilities.^{21,22} Furthermore, statistically significant rank/order correlations between CO, TUHC and various measures of PIC emissions were observed at a few sites (cf. Table 3).¹ This is encouraging considering the limited range of conditions tested and the number of data points available.

However, the simplistic concept that the extreme stability (slow destruction kinetics) of CO makes it a suitable PIC surrogate is complicated by the fact that it does not recognize the formation kinetics of CO versus organic PICs. Under some failure conditions, PIC yields may be high while CO formation has yet to reach its maximum.²³

Hypothesis 6 - Surrogates that are indicative of poor waste/air mixing, viz. benzene emissions rate, stack O₂ concentration, and waste/heat load, are indicators of PIC emissions

Rank-order statistical analyses of full-scale results have revealed that some facilities show a significant positive correlation between PIC emission rate and the following independent variables: normalized benzene emission rate, normalized toluene emission rate, waste or heat load, and the stack oxygen concentration (cf. Table 3).¹ Each of these parameters is indicative of poor mixing of waste and air, resulting in poor combustion.

Benzene and toluene are PICs expected to be formed under oxygen-deficient conditions. High waste or heat loads are indicative of system overloads such that there is not sufficient air or time for complete mixing on the molecular level. The direct correlation between stack O₂ concentration and PIC emissions was unexpected, but is apparently an indicator² of unburned O₂ due to poor waste/air mixing. Although these correlations were not observed for every facility and were not always highly significant (i.e., 80 and 90% confidence intervals) they were the strongest observed in these comparisons.

WHAT WE DON'T KNOW

There are clearly a number of issues concerning PICs that remain to be resolved.

Issue 1 - Lack of carbon and chlorine mass balance

Even the most detailed, complete full-scale studies have only accounted for about 70% of the unburned waste/fuel feed including all facility effluents.^{21,24} It is not clear whether this unaccounted material resides in the bottom ash, APCD ash, stack effluent, or other possible effluent streams. Although it is tempting to attribute this deficiency to analytical uncertainties, it may also be true that our sampling and analytical methodologies are not sufficient to detect all PICs being emitted from the facility. Closer scrutiny must be placed on determining total yields of a potential multitude of trace species that may account for the mass balance deficiency.

Issue 2 - Are high and low molecular weight PICs being fully characterized?

These species represent special sampling and analytical difficulties. High resolution capillary chromatography and liquid chromatography may be needed for analysis of high molecular weight species, while gas-absorption chromatography is necessary for very low molecular weight PICs. Research has shown that high

TABLE 3

Selected Statistical Rank-Order Correlations for Full-Scale
Hazardous Waste Incinerators

KEY:

blank = not attempted,
otherwise, # correlations / # attempts

* indicates '-' correlation coefficients
" denotes that there were '+' and
.. correlation coefficients

	O 2	C O	T U H C	B Z E M I S S	BZ + TOL E M I S S
	S T R A T E G Y	S T R A T E G Y	C O L D	C O N C	C O N C
TOTAL PIC EMISSION RATE (ug/min)	0/1	0/1	0/1	1/1	0/1
TOTAL PIC EMISSION CONCENTRATION (ug/dscm)	0/1	1/1*	0/1	1/1	0/1
TOTAL PIC EMISSION CONCENTRATION (10% O ₂)	0/1	1/1*	0/1	1/1	0/1
% PIC EMISSION / POHC INPUT	0/1	1/1*	0/1	0/1	2/2
% PIC EMISSION / WASTE INPUT	0/1	1/1*	0/1	2/2	1/1
TOTAL CHLORINATED PIC EMISSION RATE (ug/min)	2/4	0/1	1/1	1/1	0/1
TOTAL CHLORINATED PIC EMISSION CONCENTRATION (ug/dscm)	2/4	0/1	1/1	1/1	0/1
TOTAL CHLORINATED PIC EMISSION CONCENTRATION (10% O ₂)	2/4	0/1	1/1	2/2	0/1
% CHLORINATED PIC EMISSION / CHLORINATED POHC INPUT	1/4	0/1	0/1	2/2	0/1
% CHLORINATED PIC EMISSION / CHLORINATED WASTE INPUT	2/4	0/1	1/1	1/1	0/1
PIC : POHC RATIO	0/1	0/1	0/1	0/1	1/1
BENZENE EMISSION RATE (ug/min)	0/1	0/1	0/1		
BENZENE EMISSION CONCENTRATION (ug/dscm)	1/1	0/1	0/1		
BENZENE EMISSION CONCENTRATION (10% O ₂)	1/1	0/1	0/1		
% BENZENE EMISSION / POHC INPUT	0/1	0/1	0/1		
% BENZENE EMISSION / WASTE INPUT	1/1	0/1	0/1		
TOLUENE EMISSION RATE (ug/min)	0/1	0/1	0/1		
TOLUENE EMISSION CONCENTRATION (ug/dscm)	0/1	0/1	0/1		
TOLUENE EMISSION CONCENTRATION (10% O ₂)	0/1	0/1	0/1		
% TOLUENE EMISSION / POHC INPUT	1/1*	0/1	0/1		
% TOLUENE EMISSION / WASTE INPUT	0/1	0/1	0/1		
TRICHLOROMETHANE EMISSION RATE (ug/min)	0/1	0/1	0/1	0/1	0/1
TRICHLOROMETHANE EMISSION CONCENTRATION (ug/dscm)	0/1	0/1	0/1	0/1	0/1
TRICHLOROMETHANE EMISSION CONCENTRATION (10% O ₂)	0/1	0/1	0/1	0/1	0/1
% TRICHLOROMETHANE EMISSION / POHC INPUT	0/1	0/1	0/1	0/1	0/1
% TRICHLOROMETHANE EMISSION / WASTE INPUT	0/1	0/1	0/1	0/1	0/1
CHLOROMETHANE EMISSION RATE (ug/min)	1/1*	0/1	0/1	0/1	0/1
CHLOROMETHANE EMISSION CONCENTRATION (ug/dscm)	1/1*	0/1	0/1	0/1	0/1
CHLOROMETHANE EMISSION CONCENTRATION (10% O ₂)	0/1	0/1	0/1	0/1	0/1
% CHLOROMETHANE EMISSION / POHC INPUT	1/1*	0/1	0/1	0/1	0/1
% CHLOROMETHANE EMISSION / WASTE INPUT	0/1	0/1	0/1	0/1	0/1
DICHLOROMETHANE EMISSION RATE (ug/min)					
DICHLOROMETHANE EMISSION CONCENTRATION (ug/dscm)					
DICHLOROMETHANE EMISSION CONCENTRATION (10% O ₂)					
% DICHLOROMETHANE EMISSION / POHC INPUT					
% DICHLOROMETHANE EMISSION / WASTE INPUT					
1,3-DICHLOROBENZENE EMISSION RATE (ug/min)					
1,3-DICHLOROBENZENE EMISSION CONCENTRATION (ug/dscm)					
1,3-DICHLOROBENZENE EMISSION CONCENTRATION (10% O ₂)					
% 1,3-DICHLOROBENZENE EMISSION / POHC INPUT					
% 1,3-DICHLOROBENZENE EMISSION / WASTE INPUT					
CHLOROBENZENE EMISSION RATE (ug/min)					
CHLOROBENZENE EMISSION CONCENTRATION (ug/dscm)					
CHLOROBENZENE EMISSION CONCENTRATION (10% O ₂)					
% CHLOROBENZENE EMISSION / POHC INPUT					
% CHLOROBENZENE EMISSION / WASTE INPUT					
TRICHLOROETHENE EMISSION RATE (ug/min)	0/1			0/1	0/1
TRICHLOROETHENE EMISSION CONCENTRATION (ug/dscm)	0/1			0/1	0/1
TRICHLOROETHENE EMISSION CONCENTRATION (10% O ₂)	0/1			0/1	0/1
% TRICHLOROETHENE EMISSION / POHC INPUT	0/1			0/1	0/1
% TRICHLOROETHENE EMISSION / WASTE INPUT	0/1			0/1	0/1
PENTACHLOROETHANE EMISSION RATE (ug/min)					
PENTACHLOROETHANE EMISSION CONCENTRATION (ug/dscm)					
PENTACHLOROETHANE EMISSION CONCENTRATION (10% O ₂)					
% PENTACHLOROETHANE EMISSION / POHC INPUT					
% PENTACHLOROETHANE EMISSION / WASTE INPUT					
1,1,1-TRICHLOROETHANE EMISSION RATE (ug/min)	0/1	0/1	0/1	0/1	0/1
1,1,1-TRICHLOROETHANE EMISSION CONCENTRATION (ug/dscm)	0/1	0/1	0/1	0/1	0/1
1,1,1-TRICHLOROETHANE EMISSION CONCENTRATION (10% O ₂)	0/1	0/1	0/1	0/1	0/1
% 1,1,1-TRICHLOROETHANE EMISSION / POHC INPUT	0/1	0/1	0/1	0/1	0/1
% 1,1,1-TRICHLOROETHANE EMISSION / WASTE INPUT	0/1	0/1	0/1	0/1	0/1
1,1-DICHLOROETHENE EMISSION RATE (ug/min)					
1,1-DICHLOROETHENE EMISSION CONCENTRATION (ug/dscm)					
1,1-DICHLOROETHENE EMISSION CONCENTRATION (10% O ₂)					
% 1,1-DICHLOROETHENE EMISSION / POHC INPUT					
% 1,1-DICHLOROETHENE EMISSION / WASTE INPUT					
VINYL CHLORIDE EMISSION RATE (ug/min)					
VINYL CHLORIDE EMISSION CONCENTRATION (ug/dscm)					
VINYL CHLORIDE EMISSION CONCENTRATION (10% O ₂)					
% VINYL CHLORIDE EMISSION / POHC INPUT					
% VINYL CHLORIDE EMISSION / WASTE INPUT					

molecular weight PICs are numerous but are usually present in very low concentrations.²⁵ This further exacerbates the analytic problems. Quantitative trapping and recovery of low molecular weight PICs (e.g., chloromethane, phosgene) is the major problem that must be addressed to achieve a complete emissions characterization.

Issue 3 - What are environmentally acceptable PIC emission rates?

This is of course a key issue and probably the most complex. Because many PICs may be formed in ultra-trace concentrations, we may never identify all possible PIC emissions and thus never be able to ascertain the biological activity of hazardous waste incinerator emissions. Since some species may act as activators, promoters, or inhibitors of biological activity of other species, a precise knowledge of all PICs would be necessary to accurately evaluate the influence of PICs on human health.

Issue 4 - What is the relative health risk associated with PICs from different sources?

Since the evaluation of the biological activity of PICs from hazardous waste incinerators may be prohibitively time-consuming and expensive, it would be wise to be sure we are focusing on the most serious offender. Sufficient PIC data has not been obtained on a wide range of stationary combustion sources (e.g., municipal incinerators, sewage sludge incinerators, medical waste incinerators, coal and oil fired power plants, or other industrial processes) to determine which source results in the greatest environmental insult. It will be necessary to retest these sources using consistent sampling and analytical procedures, searching for the same PICs before we will truly know their relative environmental impact. Only then can we focus our energies on the sources of the most serious environmental problems.

CONTROL IMPLICATIONS

Based on a review of theoretical, laboratory, and full-scale results in combination with the failure mode theories of PIC emissions, several concepts have been identified for consideration for development into PIC control strategies. Although many of these ideas have been previously proposed, sufficient research has now been completed such that these concepts can be implemented with a firmer scientific basis. We have divided these potential strategies into design, operation, and regulatory control implications as follows:

Design Implications

- Enhanced waste/air micro-mixing
- Plug flow conditions in post flame zones
- Positive temperature gradient in high-temperature zones
- Slow quenching in cool zones

Operation Implications

- Low concentration of direct chlorinated PIC precursors
- Low Cl:H ratios in the waste or waste/fuel mixture
- Waste homogenization to remove high chlorine pockets

Regulatory Implications

- Comprehensive emission modeling
- Test burn sampling for key ToP-PICs

● Continuous monitoring of PICs

In conclusion, we briefly discuss the regulatory PIC control implications. It now seems feasible to establish a reaction kinetic data base that can be used to model and predict the relative emission rates of residual POHCs and PICs from full-scale systems. Limited trial burn emissions testing on a few "calibration" PICs can then be used to convert these relative emission rates into quantitative emissions estimates for "all" PICs and residual POHCs. These emissions estimates can be used in conjunction with available potency data to conduct risk assessments to ensure regulatory compliances. Even when the appropriate toxicological data is not available, this approach can still be used to establish a list of target PICs for trial burn testing. Such data is also invaluable to the toxicological community who must ultimately determine the potency of specific pollutants. This approach may also drive the development of reliable and appropriate PIC continuous monitors.

Credit

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PARAMETRIC EVALUATION OF METAL PARTITIONING AT
THE U.S. EPA INCINERATION RESEARCH FACILITY

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ABSTRACT

Two series of tests were performed at the U.S. EPA Incineration Research Facility (IRF) to evaluate the fate of trace metals fed to a pilot-scale rotary kiln incinerator, as a function of incinerator operating temperatures and feed chlorine content. The two series were similar in all respects with the exception of the device used for particulate and acid gas control. In the first series, the primary air pollution control device (APCD) consisted of a venturi scrubber followed by a packed column scrubber. In the second series, an ionizing wet scrubber was evaluated as the primary APCD.

Synthetic waste formulations contained five hazardous trace metals (arsenic, barium, cadmium, chromium, and lead) and four nonhazardous trace metals (bismuth, copper, magnesium, and strontium) spiked onto a clay absorbent material. Test variables were waste feed chlorine content (0, 4 and 8 percent), kiln temperature (816°, 871° and 927°C), and afterburner temperature (982°, 1093° and 1204°C).

A number of conclusions were made from the results of the first test series. Cadmium, lead and bismuth are relatively volatile, based on normalized discharge distribution data; less than 32 percent of their discharge was accounted for by kiln ash. Barium, copper, strontium, chromium and magnesium are relatively nonvolatile; more than 75 percent of their discharge was in the kiln ash. Average apparent scrubber efficiency for the individual metals ranged from 32 to 88 percent; scrubber efficiency for the three volatile metals was lower than that for five of the six nonvolatile metals. Both kiln ash partitioning and scrubber efficiency appear to be impacted negatively by increases in feed chlorine content and, to a lesser extent, increases in kiln temperature. With the exception of arsenic, discharge distributions of the metals correlate strongly with volatility temperatures.

Data from the second test series are currently being evaluated. Preliminary review indicates that the results generally support the conclusions of the first test series.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Metals, such as arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, and zinc are of concern in waste incineration because of their presence in many hazardous wastes and because of possible adverse health effects from human exposure to emissions. Incineration will change the form of metal fractions in waste streams, but it will not destroy the metals. As a result, metals are expected to emerge from the combustion zone essentially in the same total quantity as the input. The principal environmental concern centers around where and in what physical or chemical form the metals end up in the combustion system, i.e., bottom ash, air pollution control device (APCD) residues, or stack emissions.

Most interest has traditionally focused on stack emissions of metals. However, increasing attention is being given to the quality of residuals from incineration of metal-bearing wastes since disposal of these materials is becoming subject to restrictions on land disposal under the Hazardous and Solid Waste Act of 1984 (HSWA) (1).

A major role of the U.S. EPA Incineration Research Facility (IRF) in Jefferson, Arkansas is to perform research in support of regulatory development by the U.S. EPA Office of Solid Waste (OSW). Accordingly, the IRF has conducted research to study the partitioning of trace metals during the incineration of a metal-bearing surrogate waste (2). The testing described herein took place in the Rotary Kiln System (RKS) of the IRF.

PURPOSE

Field studies to date indicate that emissions of metals from incinerators burning wastes of relatively low metal content probably do not pose an unacceptable level of risk. However, as the level of metals in wastes which are incinerated rises, there is concern that some incinerators could create unacceptable risk. Current regulatory thinking suggests implementation of metal emission limits and metal feedrate limits, calculated using health risk levels and dispersion modeling.

Information gathered from the subject research will be used to further examine the impact of metals upon environmental emissions and to assist in developing and refining regulatory strategies for dealing with such an impact (3).

The research was designed to identify:

- the distribution of metal emissions among kiln ash, scrubber blowdown water, flue gas particulate and flue gas vapor
- the sensitivity of metal fate to RKS operating conditions
- the dependence of metal emissions on chlorine content of the incinerated organic waste
- the collection efficiency of several air pollution control devices (APCDs) for the metals.

This testing was conducted in conjunction with the development of a metal partitioning model under an independent EPA contract; data from these tests will be used in part to evaluate the predictive capability of the model.

APPROACH

As indicated in Figure 1, the RKS consists of a rotary kiln primary combustion chamber followed by an afterburner. Combustion gases exiting the afterburner are quenched after which they enter a primary air pollution control system. In the first of two test series, this system consisted of a venturi scrubber and packed column scrubber. In the second test series, an ionizing wet scrubber (IWS) was substituted as the primary APCD. Hereafter, the first and second test series will be referred to as the "venturi" and "IWS" test series, respectively. During both series, primary air pollution control was followed by a secondary system consisting of a carbon bed adsorber and a high efficiency particulate filter.

The feed material consisted of synthetic waste formulations mixed into a clay absorbent material. In each of the four-week series of parametric tests, metals in an aqueous solution were spiked onto the solid material, which was then screw-fed to the RKS.

The tests examined the fate of the hazardous constituent trace elements arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), and barium (Ba). In addition, the nonhazardous elements copper (Cu), magnesium (Mg), bismuth (Bi), and strontium (Sr) were spiked onto the test feed to establish whether their discharge distributions were comparable to those for the hazardous elements. In addition to the metals, toluene, chlorobenzene, and tetrachloroethylene were added to the solid material in predetermined amounts to achieve the necessary chlorine levels and heat content in the feed.

Kiln temperature, afterburner temperature and the chlorine content of the organic liquid were varied based on a factorial experimental design for three variables over three levels. The target values for the three variables were: feed liquid matrix chlorine content (0, 4 and 8 percent); kiln temperature (816°, 871° and 927°C [1500°, 1600° and 1700°F]); and afterburner temperature (982°, 1093° and 1204°C [1800°, 2000° and 2200°F]).

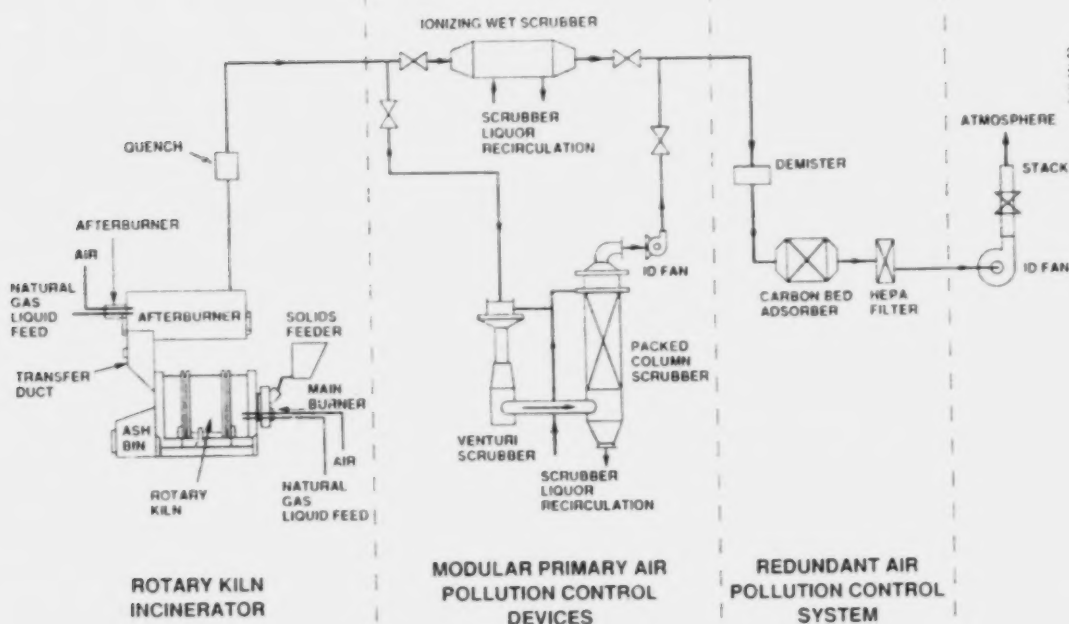


Figure 1. Schematic of the rotary kiln system

Table 1 gives the values for each of the test variables for seven test points specified by the design algorithm. The eighth test point represents a duplicate of Test Point 4. This duplicate test condition was added to provide information on test measurement precision in both test series, and was a component of a trial burn undertaken during the IWS test series. Test Point 9 provided the final component of the triplicate measurements for the trial burn.

Table 2 lists the feed concentrations of each of the metals. These values represent the sum of metals in the spike solution and background levels of metals in the clay.

All tests were conducted at the same nominal kiln exit flue gas oxygen (12%), afterburner exit flue gas oxygen (7.5%), and synthetic waste feedrate (63 kg/hr [140 lb/hr], of which 18 kg/hr (40 lb/hr) was the organic liquid matrix). For all tests, the kiln rotational speed was held constant at 0.2 rpm, and the primary APCDs were operated at their nominal design settings.

Sampling for each test included:

- a composite sample of all feed material (clay/organic liquid mixture just before kiln introduction, and aqueous metal spike solution)

- samples of scrubber blowdown water over time
- composite samples of kiln ash from each test
- samples of the flue gas at the afterburner and scrubber exits for metal capture in the particulate and backup impinger train
- samples of the flue gas at the afterburner and scrubber exits for volatile organic hazardous constituents (2).

Table 1. Parametric test design conditions.

Test	Feed Cl Content (wt %)	Kiln Exit Temp, °C (°F)	Afterburner Exit Temp, °C (°F)
1	0	871 (1,600)	1,093 (2,000)
2	4	816 (1,500)	1,093 (2,000)
3	4	927 (1,700)	1,093 (2,000)
4	4	871 (1,600)	1,093 (2,000)
5	4	871 (1,600)	1,204 (2,200)
6	4	871 (1,600)	982 (1,800)
7	8	871 (1,600)	1,093 (2,000)
8 ^a	4	871 (1,600)	1,093 (2,000)
9 ^b	4	871 (1,600)	1,093 (2,000)

^aTest Point 8 is a duplicate of Test Point 4.

^bTest Point 9 is a triplicate of Test Point 4 and was added for trial burn purposes in the IWS test series only.

Table 2. Nominal feed metal concentrations.^a

Metal	Concentration (ppm)
Arsenic	50
Barium	50
Bismuth	180
Cadmium	10
Chromium	90
Copper	500
Lead	50
Magnesium	17,000
Strontium	300

^aBased on average clay matrix metals concentrations of: Bi (12 ppm); Cr (53 ppm); Pb (3 ppm); Mg (2.2 percent); Sr (34 ppm).

RESULTS

Evaluation of the results of the venturi test series has been completed. Table 3 represents a summary of metal discharge distribution data collected during the eight-test series. Analysis of data from the IWS test series is not yet complete. Results from that series are therefore not presented herein; this discussion focusses only on the results of the venturi test series.

TEST CONDITIONS

Actual test conditions achieved were very close to target test conditions for all test points except Point 2. The average afterburner exit temperature was approximately 22°C lower than the target temperature of 1093°C for this test. For all other parametric tests, average actual operating temperatures were within 10°C of target conditions.

Actual feed chlorine content was 0 percent for Test 1; 8.3 percent for Test 7; and ranged from 3.4 to 4.6 percent for Tests 2 through 6, and Test 8.

METAL DISCHARGE DISTRIBUTIONS

Metals exiting the kiln followed one of three pathways; they either left in the kiln ash, or traveled to the afterburner with fly ash or as volatilized compounds. In this discussion, a distinction is made between volatile and nonvolatile (or refractory) metals. These are relative terms based on the amount of each metal found in the kiln ash, as a percentage of the total metal measured among the process streams (ash, scrubber blowdown, and flue gas). An assumption in making these distinctions is that metals traveling from the kiln to the afterburner are predominantly the result of volatilization, rather than entrainment in fly ash.

Cadmium, lead, and bismuth appeared to be the most volatile of the nine metals over the range of kiln temperatures tested, with average partitioning to the kiln ash of <15, 20, and 32 percent of the measured amounts for each of the three metals, respectively.

Barium, copper, strontium, arsenic, chromium, and magnesium were relatively nonvolatile, with average partitioning of 77, 79, 89, 91, 93, and 99 percent to the kiln ash for each of the metals, respectively.

In Figure 2, the discharge distribution data of each of the metals is plotted versus their volatility temperatures (the temperatures at which the vapor pressure of the most volatile principal species of each metal under oxidizing conditions is 10^{-6} atm). With the exception of arsenic, the distribution of the metals correlates strongly with that which would be predicted by volatility temperatures. The fact that arsenic is significantly less volatile than expected suggests that either a refractory compound is preferred over the predominant arsenic species (As_2O_3), or that some chemical interaction, such as strong adsorption to the clay, occurred (4).

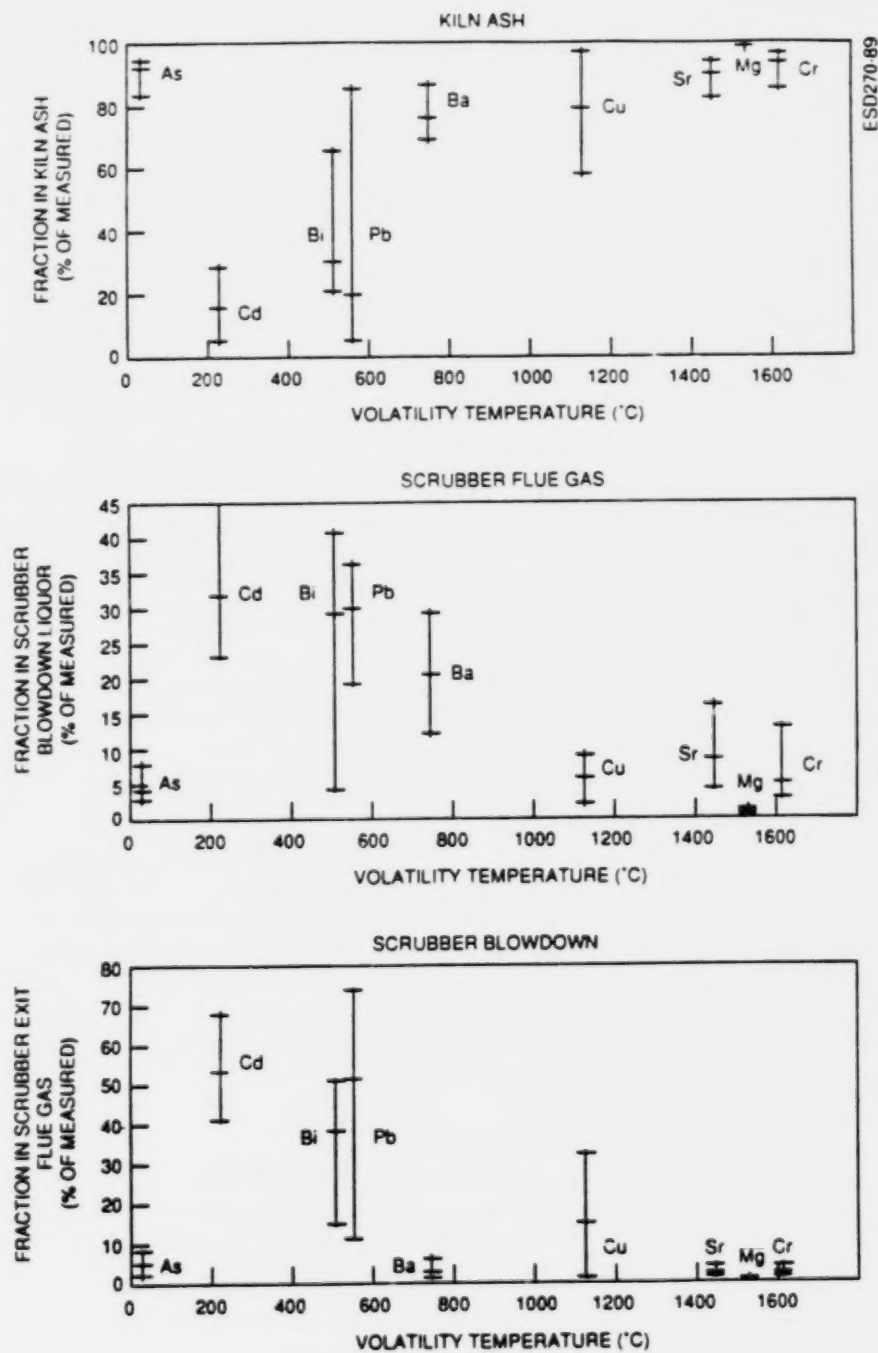


Figure 2. Distribution of metals in discharge stream.

PARAMETRIC EFFECTS

Kiln Ash Partitioning

The only metals for which kiln ash partitioning appeared to be affected by changes in kiln temperature were the most volatile metals (cadmium and lead) and arsenic. For these three metals, slight decreases in kiln ash fractions were seen with increasing kiln temperature. Kiln temperature effects for the other individual metals, as well as for total metals, were not significant within data variability.

The effect of increasing feed chlorine content on the partitioning of metals appeared to be much more significant than that of kiln temperature. As kiln and afterburner temperatures were held constant, and feed chlorine content increased from 0.0 to 8.3 percent, the overall fraction of metals partitioning to the kiln ash dropped from 81 to 63 percent.

Kiln ash partitioning of the three volatile metals decreased measurably as chlorine content rose. In the case of bismuth, the fraction of the measured metal found in the kiln ash dropped from 65 to 36 percent as feed chlorine concentration increased from 0.0 to 8.3 percent. Kiln ash fractions of cadmium and lead dropped from 29 to 9 percent, and from 84 to 6 percent, respectively, over the same chlorine range.

Only one of the refractory metals showed an increase in volatility with increasing feed chlorine content. The fraction of measured copper found in the kiln ash dropped from 98 to 58 percent as feed chlorine increased. The volatility of the other refractory metals appeared relatively stable with increasing feed chlorine.

Scrubber Efficiency

The split of metals between scrubber exit gas and scrubber water determines the apparent scrubber efficiency, defined as the ratio of metals in the water to the sum of the metals in the two splits.

Scrubber efficiency for total metals ranged from 33 to 56 percent, and to a slight extent was negatively impacted by increases in kiln temperature and feed chlorine content.

Average scrubber efficiencies for the individual metals ranged from a low of 32 percent for copper to a high of 88 percent for barium. Average scrubber efficiency for the three volatile metals was lower than that for five of the six nonvolatile metals.

Kiln temperature effects on scrubber efficiency were measurable in the cases of two of the volatile metals. Decreases in scrubber efficiency, from 51 to 31 percent for cadmium and from 42 to 25 percent for lead, were seen with increases in kiln temperature from 825°C to 927°C. This is consistent with the changes in volatilization of these metals experienced with changes in kiln temperature.

The effect of chlorine on scrubber efficiency for individual metals was significant for copper, arsenic, bismuth, and cadmium. In each case, the effect of increasing feed chlorine was to decrease scrubber efficiency. Decreases were as follows: copper (from 67 to 21 percent); arsenic (67 to 38 percent); cadmium (46 to 26 percent); and bismuth (55 to 40 percent).

The effect of afterburner temperature on scrubber efficiency for individual metals was less substantial than that of kiln temperature and feed chlorine content. Modest increases in scrubber efficiency were seen along the increasing afterburner temperature range for bismuth and lead.

Flue Gas Phase Distribution

Standard Method 5 trains were used to collect samples of flue gas particulate- and vapor-phase metals. In this discussion, two assumptions regarding this sampling technique are made: (1) all particulate-phase metals are collected on the filters, and (2) all vapor-phase metals are collected in the impingers; vapor-phase metals do not condense on the filters, nor do they pass through the impingers. (In actuality, the "vapor-phase" likely includes some water-soluble metal that has wept through the filters and collected in the impingers.)

The distribution of metals in the flue gas favored the particulate phase over vapor. Average particulate phase metals as a fraction of total flue gas metals were highest for the three volatile metals, with lead at 96 percent, cadmium at 90 percent and bismuth at 84 percent. For the nonvolatile metals, the fraction of flue gas metals exiting as particulate ranged from 82 percent for copper to 31 percent for barium.

None of the test variables had a clear effect on the split of total flue gas metals between the two phases. Likewise, effects of test variables on the flue gas phase distribution for the individual metals were not significant within data variability (4).

MASS BALANCE CLOSURE

Average mass balance closures achieved around the kiln ash and scrubber discharges ranged from 48 percent for strontium to 96 percent for cadmium. Overall average closure was 71 percent. Typical trace metal mass balance closure results from past experience with combustion sources are in the 30 to 200 percent range.

CONCLUSIONS

In the subject test series, the trace metals cadmium, lead and bismuth were found to be relatively volatile, while barium, copper, strontium, arsenic, chromium and magnesium were relatively nonvolatile. With the exception of arsenic, their observed volatilities generally agree with theoretical predictions based on volatility temperature. A correlation also

existed between venturi/packed column scrubber efficiencies and metal volatility; average apparent scrubber efficiency for the metals decreased with increasing metal volatility.

Both kiln ash partitioning and scrubber efficiency appeared to be impacted negatively by increases in feed chlorine content and, to a lesser extent, increases in kiln temperature. Neither was significantly affected by changes in afterburner temperature.

In the flue gas, particulate-phase metals predominated over those in the vapor phase. Average particulate-phase metals, as a fraction of total flue gas metals, were highest for the volatile metals. No clear effects of the three test variables on flue gas phase distributions were apparent.

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SORPTION AND DESORPTION OF POHCs AND PICs IN A FULL-SCALE BOILER UNDER SOOTING CONDITIONS

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ABSTRACT

Recent EPA test results from boilers cofiring hazardous waste have indicated that unburned organics can continue to be released in stack gases after cofiring ceases, an effect which has been termed hysteresis. In those tests it appeared that both principal organic hazardous constituents (POHCs) and products of incomplete combustion (PICs) can be sorbed on soot deposits during cofiring and then desorbed after cofiring ends, but the evidence for this hysteresis effect was limited and the impact on determination of destruction and removal efficiency (DRE) was not known. The current study was designed to evaluate sorption and desorption of organics on combustion-generated soot in a full-scale boiler during cofiring, to determine unequivocally if hysteresis exists and, if so, to evaluate its effect on DRE measurement. The results will provide guidance on the RCRA trial burn protocol for boilers. A two-week test involved a series of boiler operating conditions including background measurements, cofiring of a simulated waste, soot generation, and subsequent waste-free operation to look for organics desorption. Sampling included stack testing for volatile and semivolatile organics and continuous emission monitoring of stack gases, as well as collection of soot at several locations. Preliminary conclusions are: (1) the hysteresis effect is real and is measurable under certain conditions; (2) hysteresis can be observed both in the gas phase (stack emissions) and in the solid, sorbent phase (soot); and (3) the extent of hysteresis is compound-specific, apparently relating to physical and chemical properties such as volatility or molecular size. Assessing the full impact of hysteresis upon DRE quantitation will require further evaluation. It appears possible that a DRE could be measurably affected under some conditions, but it is also likely that the effect would be much less than an order of magnitude. The duration of the trial burn and the duration of waste cofiring which precedes it are important factors in DRE measurement where soot is generated.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

EPA test results have demonstrated that industrial boilers can provide adequate thermal environments for hazardous waste destruction, achieving an average destruction and removal efficiency (DRE) of 99.998% for RCRA-listed toxic organics, i.e., principal organic hazardous constituents (POHCs) (1). Results from recent test programs, however, have shown that unburned POHCs and products of incomplete combustion (PICs) can continue to be released in the stack gases after waste cofiring ceases (2), an effect which has been termed hysteresis. In some cases, the levels of organics peaked and then tailed off for a period. Soot blowing experiments indicated

that with cleaner boiler tube surfaces, such hysteresis effect was greatly reduced. Thus it appeared that some of the POHCs and PICs can be adsorbed on soot deposited on boiler surfaces during cofiring and desorbed back into the combustion gases after waste cofiring ceases. There was some limited evidence supporting this hysteresis effect, but the impact on the determination of DRE for POHCs was not known. A full-scale test to determine unequivocally if hysteresis exists and, if so, to evaluate its effect on DRE measurements was therefore warranted. Such a test was performed under EPA Office of Toxic Substances (OTS) Contract No. 68-02-4252, Work Assignment 14.

The objective of this study was to evaluate the sorption and desorption of organic compounds on combustion-generated soot during the cofiring of hazardous organics with fuel oil in a full-scale boiler. Testing was performed by firing a watertube package boiler at very low load, under a "smoking" condition, while spiking moderate levels of hazardous organic compounds into the fuel.

The test was *not designed to enable a quantitative redefinition of DRE for boilers*, but was instead intended as a "range-finding" experiment to determine if soot sorption and desorption could be a major factor in organic emissions relative to trial burns under certain conditions. Test results will primarily be used to *provide guidance in the design of RCRA trial burns for boilers*. Evaluation of the test results should allow development of recommended guidelines on:

- Duration of waste firing at test conditions (including waste firing and POHC input) prior to initiating a trial burn, to ensure "steady-state" POHC and PIC emissions.
- Duration of trial burn necessary to accurately measure long-term DRE performance.
- Sampling and process monitoring procedures that account for soot sorption.

TEST PROTOCOL

FACILITY DESCRIPTION

Testing was conducted during September 1989 at the Tampela/Keeler (formerly Keeler/Dorr-Oliver) boiler manufacturing plant in Williamsport, Pennsylvania. A plant boiler was selected on the basis of its ability to fire either natural gas or fuel oil, its seasonal availability, and because of the cooperation and support available from the Tampela/Keeler personnel.

The test unit was a Model DS-17.5 boiler used for plant heating and test purposes, with a capacity of 17,500 lb/h (2.21 kg/s) of steam and a furnace volume of $\approx 415 \text{ ft}^3$ (11.8 m³) (see Figure 1). The unit is fired by an air-atomizing oil burner (8:1 turndown ratio) which can accommodate several fuel types, including natural gas, No. 2 fuel oil, and No. 6 fuel oil. Stack gases are monitored by oxygen (O₂) and nitrogen oxide (NO_x) analyzers and an opacity meter. The facility is not equipped with any air pollution control devices, and none is required.

Prior to testing, the boiler was cleaned and as much residual soot as possible was removed from all accessible interior surfaces. An estimated 60% of the boiler tube surface was cleaned, the remainder being physically unreachable.

EXPERIMENTAL DESIGN

Test Matrix

A variety of parameters can affect the sorption and desorption of POHCs and PICs, including boiler operating conditions (e.g., load, fuel type and firing rate, waste cofiring rate, burner turndown, excess air, combustion chamber temperature, and flue gas composition), waste characteristics (e.g., chlorine concentration and chemical

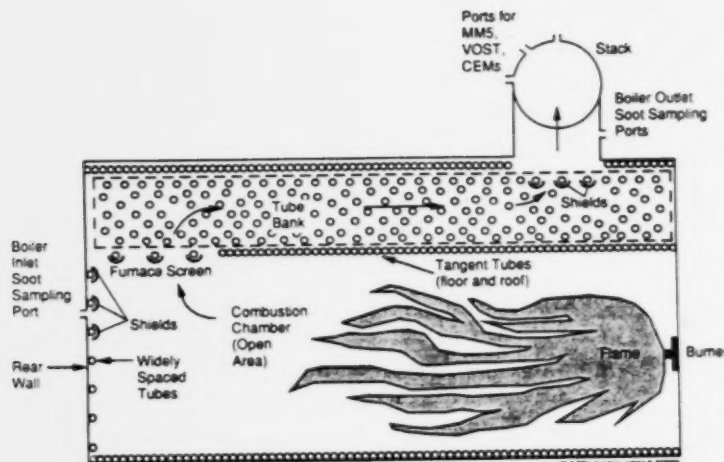


Figure 1. Keeler watertube package boiler: top view.

composition), and POHC characteristics (e.g., sorptive characteristics, thermal stability, and behavior relative to PICs). Although it was not possible to address every parameter individually, this test was designed to create conditions that were expected to allow the greatest sorption effects and then to measure those effects. During the test, operation of the boiler was deliberately altered to produce a poor combustion mode (i.e., low load and low excess air), and also nonoptimum air distribution within the burner, in order to deliberately produce soot.

Both monochlorobenzene (MCB) and trichloroethylene (TCE) were selected as POHCs on the basis of their chemical structure, thermal stability, adsorption characteristics, analytical detectability, and availability. A separate pump and metering system was set up to spike each POHC directly into the fuel oil feed line. The two POHCs and the fuel oil, which simulated a hazardous waste, were then pumped through an in-line mixer and injected into the burner.

The test program covered six different boiler operating conditions. These conditions and the associated sampling and analysis activities are summarized in Table 1. The first two conditions consisted of short background tests in which the boiler was fired with fuel only, either (1) natural gas or (2) No. 6 fuel oil.

Test condition 3 used POHCs cofired with No. 6 fuel oil under nonsooting combustion conditions. POHCs for the test series were each to be fired at 5% of the fuel oil feed rate. The test period involved one day (24 h) of continuous boiler operation with periodic sampling activities.

Test condition 4 involved cofiring the two POHCs with fuel oil under soot-producing conditions which were determined on-site. Excess air was lowered to induce soot generation. Both stack opacity readings and visual observations through boiler sight glasses confirmed the generation of soot. The test period covered two continuous days of boiler operation with periodic sampling activities.

To initiate test condition 5, the fuel was switched from fuel oil to natural gas, and POHC cofiring was ceased. The combustion furnace exit temperature was maintained at the same level as in test condition 4. Under this condition the hysteresis effects of the boiler were measured for three continuous days. The test duration was based partly upon organic levels indicated by field GC (i.e., using near-"real time" feedback).

Test condition 6 involved a final collection of soot samples after the boiler was allowed to cool. Soot sampling shields and soot scrapings taken directly from the boiler tubes were collected at this time.

TABLE 1. EXPERIMENTAL DESIGN AND SAMPLING MATRIX

Run No./test condition	Run length	Sampling methods* and frequencies				CEM/GC
		VOST	MM5	Soot	Feeds	
1. Natural gas (background)	4 h	One 40-min sample collected hourly	-	-	-	Continuous
2. No. 6 fuel oil (background)	6 h	One 40-min sample collected hourly	One 3-h sample starting 2 h into run	3 sets (1 set each from furnace and both flue locations) collectors removed from probes 3 h into run; probes returned to sampling position	One grab sample of fuel oil	Continuous
3. No. 6 fuel oil with POHCs cofiring (nonsooting)	24 h (continuous)	One 40-min sample collected every other hour	One 8-h sample starting at beginning of run	-	One grab sample of fuel oil and each POHC	Continuous
4. No. 6 fuel oil with POHCs cofiring (sooting)	51 h (continuous) (3 h at high cofiring rate, 4 h with no cofiring, and 44 h at reduced cofiring rate)	One 40-min sample collected hourly	One 3-h sample starting at beginning of run (terminated when cofiring interrupted) and one 8-h sample starting 23 h into run	3 sets collectors removed 28 h into run; 1 set collectors removed from boiler inlet probe 48 h into run (following probe overheating)	One grab sample of fuel oil and each POHC for each day of sampling	Continuous
5. Natural gas, no POHCs (hysteresis)	73 h (continuous)	One 40-min sample collected hourly until field GC readings indicated "tail off"; then collected with diminishing frequency to end of run	Three 8-h samples starting at beginning, 20 h, and 44 h into run, respectively	2 groups of 3 sets collectors removed 4 h and 28 h into run, respectively	-	Continuous
6. Cold furnace	After furnace cooling	-	-	18 soot shields removed from boiler tubes and 9 scrapings collected	-	-

*CEM = Continuous emission monitoring for CO, CO₂, O₂, and THC (Methods 10, 3A, 3A, and 25A, respectively).

GC = Field cryogenic trap/GC/FID for POHCs (monochlorobenzene and trichloroethylene) and selected PICs.

VOST = Volatile organic sampling train for volatile POHCs and PICs (Method 0030). Two-thirds of sample pairs were combined for analysis, while one-third underwent separate trap analyses (Methods 5030, 5040, and 8240).

MM5 = Modified Method 5 for semivolatile PICs (Method 0010), analyzed by Method 8270.

Soot = Three types of samples:

1. Soot sampling water-cooled probes with clamp-on collectors. Three probes simultaneously collected soot at two sampling locations (furnace and flue). Each "set" of samples was three separate collectors from a probe. Collectors were quickly removed from the withdrawn probe and carefully stored until analysis.
2. Shields were clamped onto existing boiler tubes prior to the test for collection of soot throughout the entire test series.
3. Scrapings of soot from the existing boiler tubes were collected following the hysteresis testing.

Feeds = One fuel oil sample is to be analyzed, and additional samples will be archived. POHC samples will be archived.

Practical constraints limited the amount of soot formed. Since the test boiler was not equipped with pollution control devices, state air quality standards limited the extent of soot allowable due to a 20% stack opacity limit.

Specialized Sampling and Analysis Techniques

This project used several specialized, nonstandard sampling and analysis techniques. Discussed below are the techniques for soot sampling and analysis and the field GC used for on-site POHC monitoring.

Soot samples were collected by three methods: (1) soot collection probes designed to collect soot in the furnace and at the boiler outlet, (2) soot collection shields attached to boiler tubes, and (3) scrapings of soot from boiler tubes. Soot collection probes and shields were placed in position before the test began. The probes were withdrawn at specified times for removal of soot samples (during Runs 2, 4, and 5). Following all test activities, soot shields were removed for sample collection, and boiler tube scrapings from the same locations as the shields were also collected.

Three soot collection probes were used to collect soot and to withdraw cumulative samples at various times (see Figure 2). The probes were built with a double shell to allow ethylene glycol coolant to flow between. In this fashion, the outer wall of the probe was kept relatively cool ($\approx 300^{\circ}\text{F}$) in the hot boiler environment to thus simulate actual boiler tube surfaces.

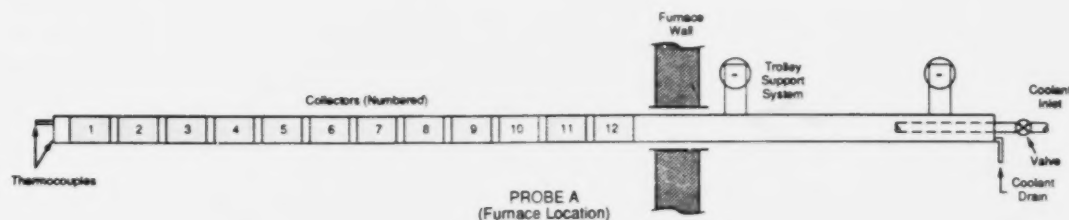


Figure 2. Soot probe schematic.

Each probe was fitted with a series of carbon steel sample collection rings ("collectors") which were clamped directly onto the probe outer shell. Volatile as well as semivolatile organic compounds adsorbed onto the soot were thus "trapped" by the relatively cool surface and were thermally desorbed during subsequent analysis. Thermocouples monitored probe surface and combustion gas temperatures. When a probe was withdrawn for taking samples, a predetermined set of collectors was retrieved as quickly as possible. Storage procedures for the soot samples were geared toward reducing loss of organics and minimizing outside contamination.

Eighteen soot collection shields, similar in size and material to the probe collectors, were mounted to selected boiler tubes in three locations: (1) along the furnace wall opposite the flame, (2) near the furnace exit, and (3) near the boiler exit. The shields collected soot throughout the entire test sequence. After the boiler cooled, the shields were retrieved, and in addition, soot was scraped from the boiler tubes in the same locations as the shields. Storage procedures for these two sample types paralleled those of the probe samples.

Three methods for the analysis of organic compounds in soot were investigated, including thermal desorption-gas chromatography/mass spectrometry (GC/MS), solvent extraction-GC/MS, and supercritical fluid extraction-GC. Thermal desorption-GC/MS was selected for test sample analysis on the basis of spike recoveries, detection limit, reproducibility, and sample size requirements. Using this technique, the soot samples were heated

ballistically in the interface chamber at the inlet of a GC/MS. Any volatile organic species thereby released were subsequently analyzed by conventional GC/MS methods. The effect of desorption temperature on POHC yield from soot was evaluated. The yield of POHCs and several hydrocarbon species observed during the soot analysis was highly temperature-dependent, and a desorption temperature of 900°C was determined to be the optimum for desorption of POHCs. These results indicate that POHCs (and other species) incorporated into the soot during the actual soot formation are tightly bound to the soot matrix. Despite the high desorption temperatures used, no POHC decomposition was observed. Method detection limits for the thermal desorption-GC/MS method were shown to be 500 pg/mg (500 ppb) and 20 pg/mg (20 ppb) of POHCs in soot for full-scan and selected-ion-monitoring modes, respectively. Method precision was determined during the analysis of the calibration curves for each POHC by each GC/MS method and found to be better than $\pm 20\%$ (relative standard deviation) in all cases. Additional details on the analysis method and its development are available in a separate method development report (3).

The field gas chromatograph (GC) used to monitor organic compounds covers a boiling point range roughly equivalent to those of C_1 to C_{17} hydrocarbons (-160°C to 300°C). It was used as an indicator to monitor boiler outlet organic levels, especially during the hysteresis "tail-off" phase, and to assist in coordinating the other sampling methods. The system allowed semicontinuous monitoring of selected organic compounds collected continuously, via their concentration in a cryogenic trap and subsequent analysis by GC/flame ionization detection (GC/FID).

The sample to the field GC was split off from a Teflon® heated line and maintained at 250°C, passed through a Perma Pure® dryer, and then injected into a liquid CO_2 -based cryogenic cooling loop. The cooling loop acted as a concentrator to enhance sensitivity, resulting in an integrated sample which could be injected periodically (roughly hourly) into the GC/FID. The GC was fitted with a megabore column and temperature-programmed to improve separation of target organic compounds. The FID was adjusted to scan for the two test POHCs and selected PICs.

Technical Considerations

Major practical limitations affected the establishment of priorities and data end use. In particular, known, validated techniques did not exist for the collection, preservation, and analysis of soot for this study, although the best procedures possible and immediately available were used to increase the likelihood of generating useful data.

Key limitations relating to the usefulness of the soot results are:

- It was *not* possible to quantitate the rate of soot generation in the test boiler because the probe-based sampling technique did not necessarily provide for representative sampling of the entire gaseous stream within the combustion chamber or boiler exit. Accordingly, the amount of total POHCs or PICs in the combustion gases that were trapped in the soot could not be quantitated. Therefore, a mass "balance" of the partitioning of organics between the solid phase (soot) and the gaseous phase (stack gases) was not possible.
- Some of the organics in the soot may have escaped prior to analysis. It was not possible to *determine* the degree of sample integrity, although it was *controlled* as well as possible. Furthermore, the efficiency of desorption of organics from soot for subsequent analysis was not known, and measurement of true recoveries was not possible. Nevertheless, the results are quite useful on a relative basis.

Considering these and other limitations, the soot testing portion was intended to provide more *qualitative* data than quantitative. An objective was to look at *trends over time* (sorption and desorption), both in the soot samples and in the stack samples. Comparison of results for each phase (i.e., solid and gas) assisted in evaluating the role that soot on boiler tubes plays in the hysteresis effect.

RESULTS

PROCESS CONDITIONS

The process operating conditions and stack gas levels for each test period are summarized in Tables 2 and 3, respectively. The combustion temperature (furnace exit temperature) was low, only $\approx 900^{\circ}$ to 1100°F , compared with typical trial burn temperatures of 1600°F or more. Although the boiler operation is not normally controlled by furnace temperature, the temperature was maintained as constant as possible.

POHC cofiring began in Run 3 at the planned rate, about 5% by volume for each POHC. The rates were reduced during Run 4 due to extremely high levels of acid gases and organics believed to be present, and because of the potential for boiler corrosion and possible VOST analysis problems, respectively. The changes in cofiring rates complicate data interpretation for organics results.

The stack flow rate ranged from 1460 to 1740 acf/min (840 to 1080 dscf/min), as measured during MMS sampling. The stack opacity levels were generally maintained under 20% by carefully controlling excess air. Table 3 summarizes the stack levels of gases as measured by CEMs.

TABLE 2. KEY PROCESS CONDITIONS

Run No./ Test condition	Approx. duration (h)	Furnace temp. ^a ($^{\circ}\text{F}$)	Nominal steam load ^b (lb/h)	Fuel flow rate ^c	POHC feed rate (lb/h)		POHC cofiring rate--volumetric basis (% total)			Opacity (%)
					TCE	MCB	TCE	MCB	Total	
1. Natural gas (background)	4	930-1130	3000	39 cfh (N.G.)	0	0	0	0	0	0 ^d
2. Fuel oil (background)	6	965-1080	3000	38 gph	0	0	0	0	0	0 ^d
3. POHC cofiring (nonsooting)	24	935-1007	3000	28 gph	16.7	12.4	4.5	4.4	8.8	6-8
4. POHC cofiring (sooting)	51	956-1061	2700	28 gph	16.8/8.8 ^e	13.2/7.4 ^e	4.5/2.5 ^e	4.6/2.7 ^e	9.1/5.2 ^e	11-22
5. Natural gas (hysteresis)	73	910-1070	2500	40 cfh (N.G.)	0	0	0	0	0	0-10

^aMonitored at soot probe positioned near boiler inlet. Note: The flue gas temperature, monitored at location of boiler outlet soot probes, ranged from 350° to 376°F .

^bNominal steam pressure was 100 psig.

^cNo. 6 fuel oil, unless noted "N.G." for natural gas.

^dSlight baseline drift observed.

^eInitially, cofiring rates for Run 4 continued at the same rates as during Run 3. After about 3 h, cofiring was stopped for about 4 h, then resumed at about 30% of the previous rate, which continued for 44 h.

TABLE 3. CONTINUOUS EMISSION MONITORING RESULTS

Run No.	Average stack concentration (range shown in parentheses)*			
	O ₂ (%)	CO ₂ (%)	CO (ppm)	THC (ppm)
1	5.0 (4.1-5.8)	8.6 (6.5-8.8)	10 (0-23)	2 (0-3)
2	5.6 (5.1-8.2)	11.5 (9.3-12.2)	64 (38-127)	2 (1-4)
3	4.8 (3.1-7.8)	12.4 (11.0-12.8)	97 (52-180)	2 (0-3)
4	2.2 (1.7-8.6)	14.5 (8.9-15.1)	626 (91-8071)	13 (1-293)
5	2.8 (0.1-11.9)	10.1 (1.4-14.9)	23 (2-828)	1 (0-26)

*All concentrations reported on a dry basis, as measured.

The oxygen (O₂) level, i.e., excess air, was reduced in Run 4 to deliberately generate soot. Since the oxygen level was manually controlled to try to maintain relatively constant stack opacity, more variation is seen in Run 4.

Carbon monoxide (CO) levels were reasonably low in Runs 1, 2, and 3, but were very high in Run 4, with a maximum of over 8000 ppm. CO was initially high in Run 5, but quickly stabilized at less than 25 ppm. The total hydrocarbon (THC) trends are somewhat similar to those of CO. THC levels were very low and varied little, except during Run 4.

STACK EMISSIONS

POHC Results

Stack gas levels of the two POHCs are shown in Figure 3 for all of the test conditions. (The inset is a "blow-up" of the hysteresis portion of the graph.) The TCE concentration was high in the initial natural gas baseline condition (Run 1), but it decreased substantially by the end of Run 2. It is possible that the boiler was initially contaminated with TCE but that the first few hours of operation essentially "burned out" the contamination. The background levels of MCB were relatively low.

When cofiring began, the POHC levels generally continued to climb during Run 3 and did not level out. The sooting condition (Run 4) began with a marked increase in stack gas POHC levels, but the levels decreased with the reduction in cofiring rate. With time, the levels generally dropped, climbed, and dropped again before the boiler feed was switched to natural gas for the hysteresis period. Some of this variation may be due to the gradual buildup of a soot layer which sorbed more and more organics from the gas stream. However, some of the more abrupt changes in concentration (i.e., "sawtooth" patterns) may be an artifact of the analysis procedures.

Throughout Runs 3 and 4, the higher level POHC switched back and forth between TCE and MCB, indicating similar but varying levels of destruction and removal.

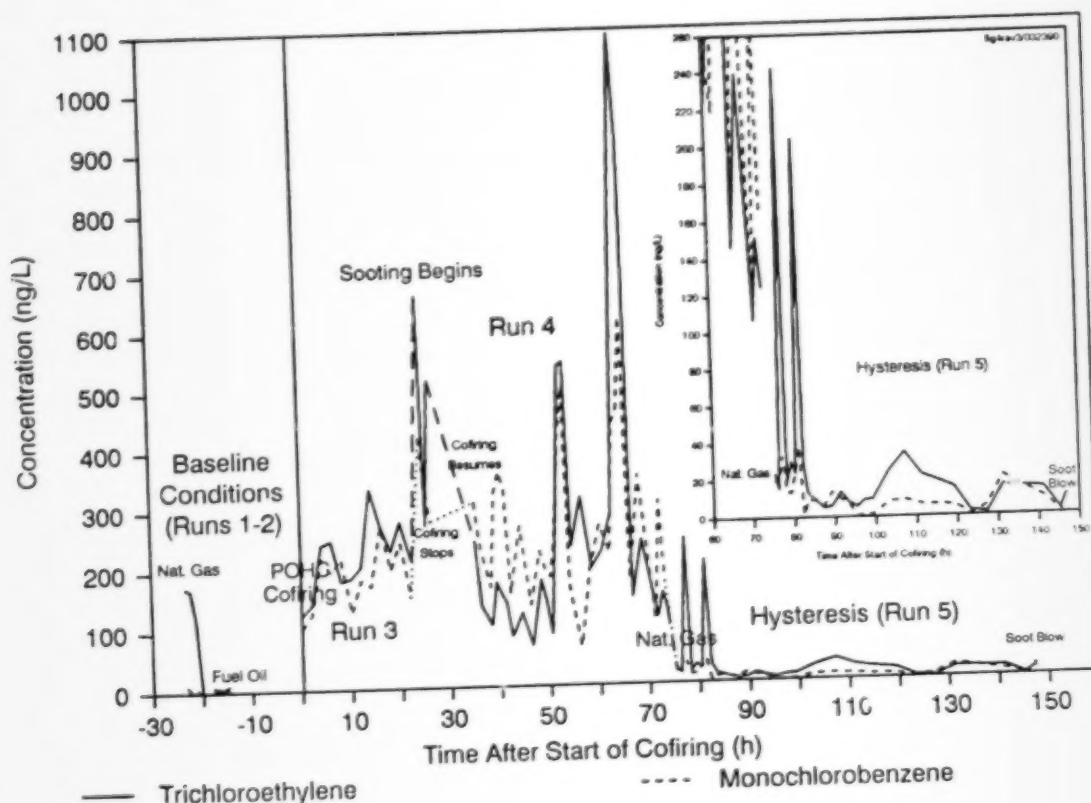


Figure 3. POHC stack gas concentrations from VOST.

The POHC levels rapidly dropped upon initiation of the hysteresis condition (Run 5). Levels generally continued to drop, then stabilized somewhat after roughly 10 hours. (The initial two high TCE peaks may be analysis artifacts. Further planned evaluation of the VOST and field GC results may help to clarify.) Later in the run, the TCE levels increased, reaching a maximum roughly 33 hours after the start of "hysteresis." Interestingly, the MCB levels increased and maximized even later, but since this increase accompanied another "peak" of TCE, this may be due to some kind of perturbation in the boiler.

At the end of the hysteresis period, soot was deliberately "blown" from the boiler bank by manually injecting steam in several pulses, to learn if the POHC and PIC levels would increase. This soot blowing episode, which lasted about 10 minutes, resulted in a minor rise of TCE, but no MCB was detected. Thus, there was not a dramatic rise in POHCs, although much of the sorbed POHCs may have already "bled off" during the 3 days after cofiring ended.

Destruction and removal efficiencies (DREs) were determined to further evaluate combustion conditions and to better relate other test results to trial burn practices. As summarized in Table 4, DREs were generally low, only three to four "nines." Interestingly, the averages were about the same for either POHC, indicating that the actual "incinerabilities" ranked about equally under these operating conditions. DREs were higher in Run 3, as expected, since oxygen had not yet been lowered. DREs were higher in the first part of Run 4, compared to the second part. This was expected, since the cofiring rate was higher, considering the generally observed trend of increasing DRE with increasing POHC concentration (4).

TABLE 4. DREs DURING POHC COFIRING

Run No.	Test condition	No. of sample pairs	Destruction/removal efficiencies (DREs): average and range (%)	
			Trichloroethylene (TCE)	Monochlorobenzene (MCB)
3	POHC cofiring/nonsooting	11	99.9947 (99.9923-99.9975)	99.9943 (99.9913-99.9974)
4a	POHC cofiring/sooting*	3	99.9904 (99.987-99.9945)	99.9913 (99.989-99.9929)
4b	POHC cofiring/sooting†	27	99.986 (99.951-99.9972)	99.987 (99.970-99.9972)

Note: The number of DRE determinations was the same as the number of VOST sample pairs for each test condition. Each DRE was based upon the POHC output rate from one VOST pair and the POHC input rate from the closest matching time period with feed data.

*Initial cofiring rate nominally the same as Run 3.

†Adjusted cofiring rate to approximately 50% that of Runs 3 and 4a.

These results show that the test was conducted on the "ragged edge" of four nines DRE, which is where any hysteresis effect would be expected to matter the most from a compliance viewpoint.

Hysteresis effect quantitation much depends upon the conditions in which the measurements were made as well as other assumptions. The test design and execution may have biased the rate of organics sorption and desorption and also the approach for measuring hysteresis. Table 5 shows the hysteresis effect, both in terms of the total mass emitted and also on a rate basis, which takes into account sampling duration. The mass values are an integration of the "area under the curve" for mass emission rates versus time. Calculating the masses of POHCs for each test condition served as a means to assess the hysteresis effect. The background amounts in Runs 1 and 2 can be compared against those in Runs 3, 4, and 5. As discussed above, the TCE levels were high in Run 1, but the TCE appeared to be largely "purged out of the system" before Run 2 began.

Assuming no sorbents for the POHCs were present prior to the deliberate soot generation in Run 4, then hysteresis involved only what was emitted in Run 5 as compared to the amount emitted in Run 4. The ratio of the mass emitted during hysteresis to the mass emitted during soot formation was calculated as 10.5% for TCE and 5.5% for MCB; however, it must be emphasized that this test was conducted as a "worst case" type experiment. The real interest is in what would happen in a typical trial burn period of about 3 to 6 hours. Continued data evaluation will focus on extrapolating results to trial burn situations.

Several key questions that relate to an assessment of the hysteresis effect will be further evaluated:

- Had the soot reached a terminal thickness? (As soot builds up on a "cool" boiler tube surface, it gradually will decrease the heat transfer between the hot gases and the much cooler boiler tube. It is expected that the outermost layer of soot particles will eventually become so hot that no more soot will tend to collect, hence, a "terminal" thickness will be reached.)
- Had the sorption and desorption processes reached "steady-state" by the end of Run 4 (i.e., was there still a net decrease of POHCs due to sorption, or had the soot reached saturation capacity)?
- What effect did varying chemical and physical characteristics of the POHCs and PICs have on their sorption and desorption?

TABLE 5. POHC MASS EMISSIONS BY TEST CONDITION

Run No.	Test condition	Duration (h) ^a	Total mass (g/run)		Emission rate (g/h)	
			TCE	MCB	TCE	MCB
1	Natural gas (background)	4.0	0.706	0.022	0.176	0.006
2	Fuel oil (background)	4.0	0.038	0.009	0.010	0.002
3	POHC cofiring/nonsooting	23.9	9.71	8.08	0.406	0.338
4a [†]	POHC cofiring/sooting	3.0	2.20	1.56	0.732	0.520
4b		40.3	18.4	17.3	0.456	0.429
4		43.3	20.6	18.9	0.475	0.436
5	Natural gas (hysteresis)	72.0	2.16	1.04	0.030	0.014
5	Soot blowing (hysteresis)	0.2	0.0029	0	0.017	0
5:4 [‡]	Mass during hysteresis versus mass during sooting		10.5%	5.5%	6.3%	3.3%

^aTimes refer to test intervals monitored by VOST, and may differ from those in Table 1.

[†]Run 4a: POHC cofiring rates matched those of Run 3.

Run 4b: Cofiring rates adjusted to 50% of those of Runs 3 and 4a.

[‡]A measure of total "hysteresis" stack POHC emissions vs. stack POHC emissions during sooting conditions.

PIC Results

PICs were monitored via both volatile and semivolatile sampling techniques. VOST samples were analyzed for two POHCs and 23 other target analytes (all were EPA Method 624 compounds). The MM5 samples were analyzed for about 20 target analytes, and in addition, major unknowns were semiquantitated. The average concentrations of PICs and POHCs are compared in Figure 4.* Total volatile PICs (i.e., all target volatile organics other than the two POHCs) were found at levels similar to the POHCs; however, benzene made up much of the total PICs.

The total concentration of semivolatile *known* PICs was less than the total (known) volatile PICs.† However, during Runs 2-4, the semivolatile unknowns were present at roughly an order of magnitude higher concentration than were the knowns. During Run 5, the semivolatile levels were quite low, and the unknowns were only about double the levels of the knowns.

*Runs 4A and 4B refer to the higher and lower cofiring rate periods of the sooting condition, whereas Run 5 is divided into three segments, "A," "B," and "C," according to when the MM5 samples were taken.

†The semivolatile data are blank corrected as applicable.

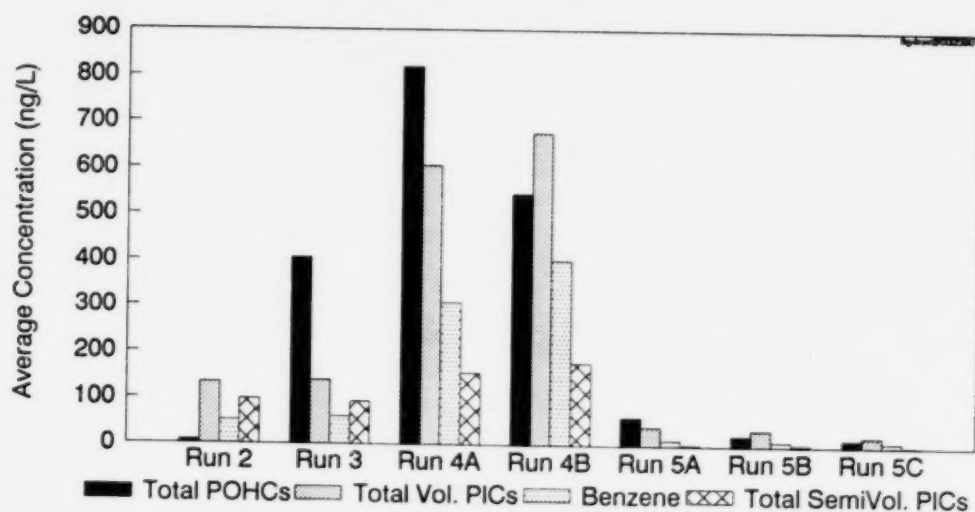


Figure 4. Average stack gas concentrations of POHCs and PICs.

The average levels of the major PICs (other than benzene) are shown in Figure 5. The highest level volatile PICs included benzene, 1,1-dichloroethylene (DCE), methylene chloride (MeCl_2), dichlorobenzenes (DCBz's, as the total of 3 isomers), and toluene. The major semivolatile PICs included naphthalene and phthalic anhydride. As seen in both Figures 4 and 5, the semivolatile PICs had a lower ratio of Run 5 concentrations to Run 4 concentrations than did the volatile PICs. This could mean either (a) the amount of semivolatiles "held up" was less, or (b) assuming similar levels were sorbed, they were released less completely in the 3-day sampling period.

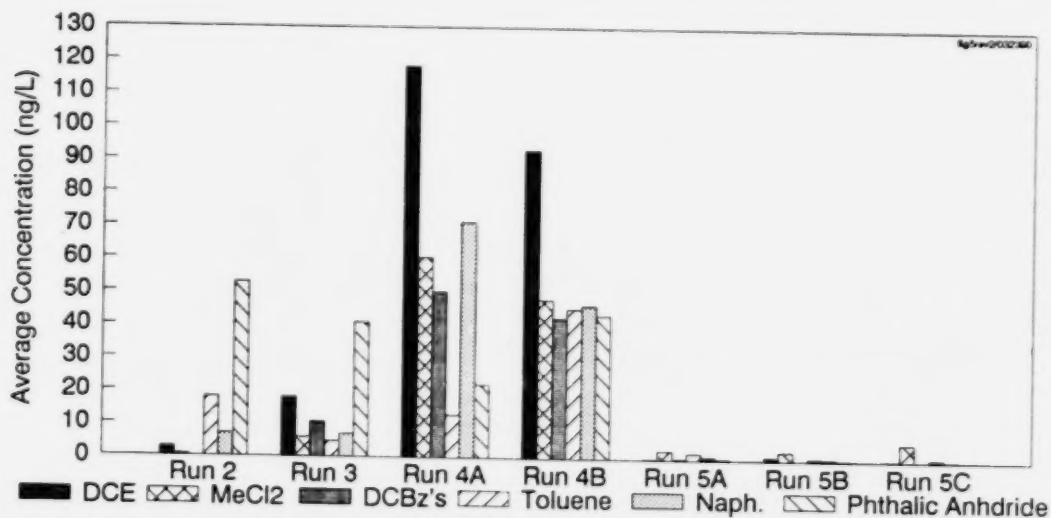


Figure 5. Average stack gas concentrations of major PICs.

Levels of some of the other PICs of significance are shown in Figure 6, including the volatile compounds 1,1,1-trichloroethane (1,1,1-TCA), chloroform (CHCl_3), and carbon tetrachloride (CCl_4), and the semivolatile compounds phenanthrene, dibenzofuran, and benzaldehyde. Again, volatiles tended to predominate during Run 5. 1,1,1-Trichloroethane was found at high levels during the background runs and may have been a contaminant in the boiler.

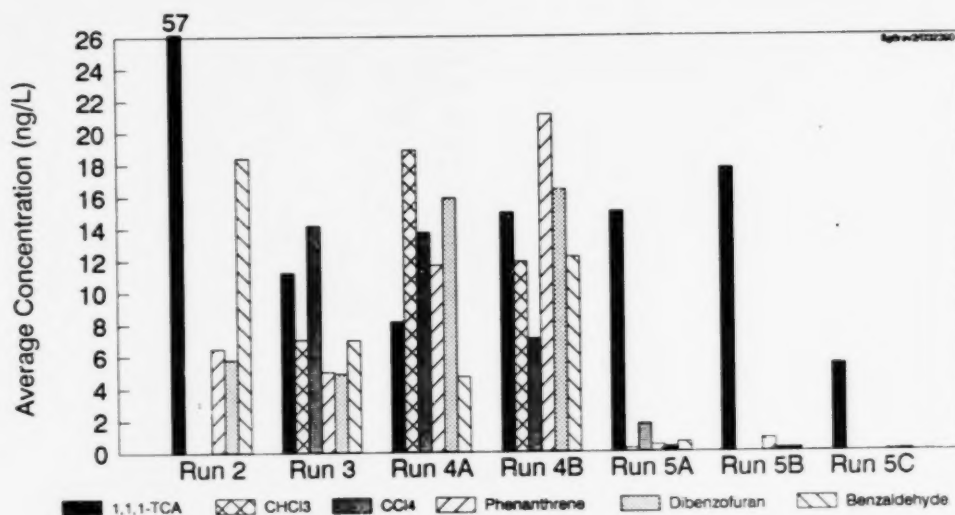


Figure 6. Average stack gas concentrations of other PICs.

Of the primary PICs discussed above, those displaying more apparent hysteresis effects (i.e., higher Run 5 concentrations as compared with Run 4 concentrations) included 1,1,1-trichloroethane, methylene chloride, carbon tetrachloride, and benzaldehyde. Benzene, toluene, chloroform, naphthalene, phenanthrene, and dibenzofuran displayed less effect, and 1,1-dichloroethylene, dichlorobenzenes, and phthalic anhydride displayed the least effect. In general, the POHCs showed more hysteresis effect than the PICs, and the volatile PICs showed more effect than did the semivolatile PICs.

The highest level PICs seen during soot blowing tended to be the more volatile compounds sampled by VOST.

SOOT RESULTS

Figure 7 shows the levels of POHCs found in the soot probe samples. Levels of POHCs in the background samples from Run 2 were very low. (Only samples from the boiler inlet probe were analyzed since no soot was expected to be present. It is likely that the small amount collected was a different type of material than was collected during Runs 4 and 5.) TCE and MCB were found at similar levels in Run 4 samples, the sooting condition.

During Run 4, the boiler inlet probe overheated (from nominally 300°F to over 700°F) between the 28-hour and the 48-hour samples. The latter sample was collected to determine whether soot on that probe had built back up organic levels, assuming that the overheating had caused a loss. It can be seen that the levels at the end of Run 4 did essentially match those of the first sample set collected in Run 4.

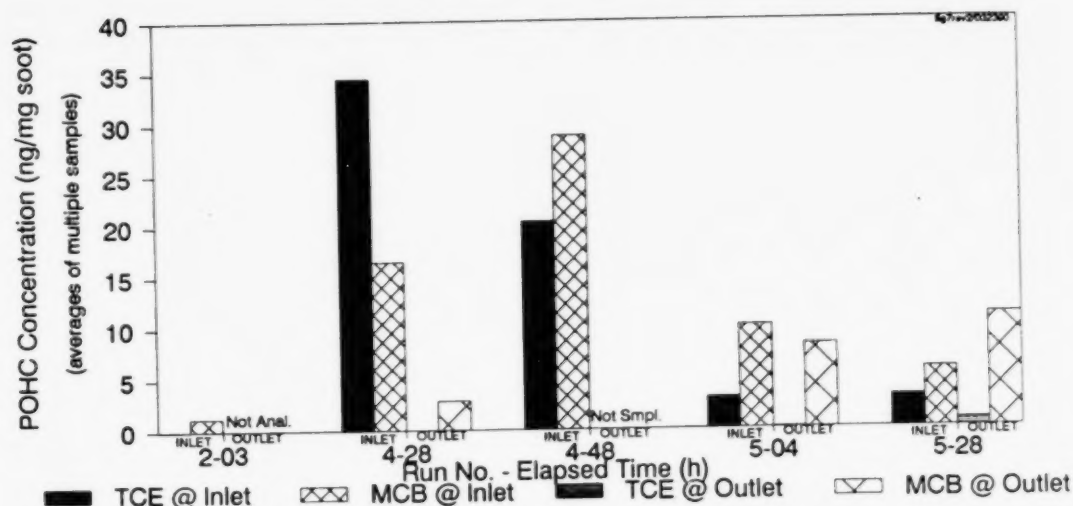


Figure 7. POHC results from soot probe samples.

The hysteresis effect can be evaluated from the soot samples as follows: for the boiler inlet, compare the "4-48" sample results with the Run 5 sample results; whereas for the boiler outlet, compare the "4-28" sample results with the Run 5 results. The Run 2 results can be misleading since a different type of material was likely collected and much less of the material was present than in the Runs 4 and 5 samples. This applies also to the PIC data, which are discussed below.

Stack gas results indicated that more TCE was emitted during the hysteresis period than was MCB; in fact, roughly double the amount was emitted (refer to Figure 3 and Table 5). The soot results show some trends consistent with the stack gas results. Comparing Runs 4 and 5, the TCE levels dropped much more at the boiler inlet than did the MCB levels. Actually, MCB appears to be "held up" more in the soot, as further evidenced by the marked "delayed" increase in MCB levels in the boiler outlet soot during the time period of Runs 4 and 5. TCE also rose in the outlet soot, but not as much. All of this behavior is consistent with the physical characteristics of the two POHCs (e.g., volatility and molecular weight).

The soot PIC data show similar trends, but actual concentrations cannot be compared because only relative units were appropriate according to the analysis procedure.* (Refer to Figures 8 and 9; units are in mg^{-1} .) Analytes included only a limited number of preselected PICs. For those PICs the following order was observed: in order of decreasing relative concentration, toluene > benzene > naphthalene > xylenes (total of 3 isomers) > dichlorobenzenes (total of 3 isomers) > 1,1-dichloroethylene (DCE). With the exception of DCE, in comparing

*Each PIC was quantitated by computing the relative peak area for the PIC with respect to the peak area for the internal standard (IS), chlorobenzene- d_5 , and to the total soot mass. In other words, a unitless ratio of peak areas was divided by the mass of the soot aliquot which was analyzed. The units are mg^{-1} . This method of quantitation was chosen for three reasons. First, the variability in the results precludes accurate absolute quantitation. Second, no standards for the PICs were used so no relative response information was available. Finally, the mass spectrometry data were collected in the selected-ion-monitoring mode (SIM), so that an assumption of a response factor of 1.0 relative to the IS would likely be in error by as much as a factor of 20.

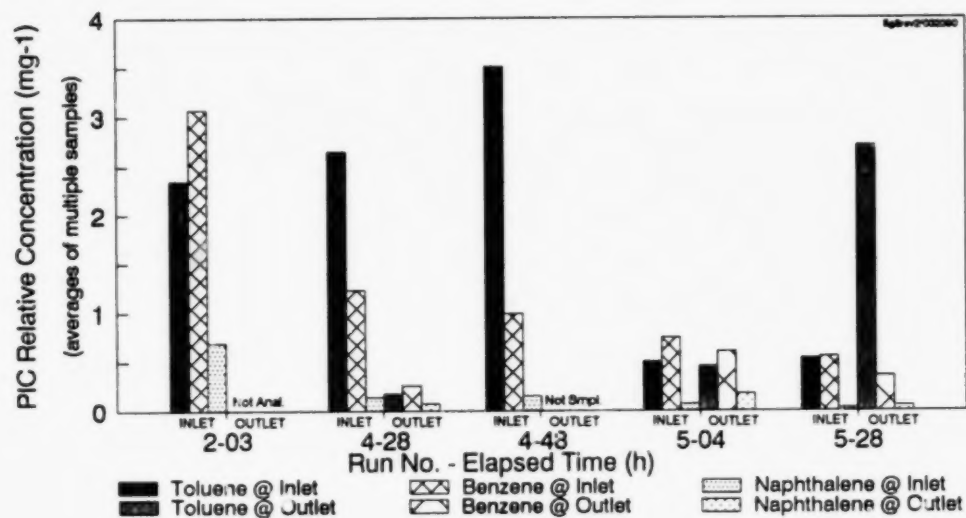


Figure 8. Major PIC results from soot probe samples.

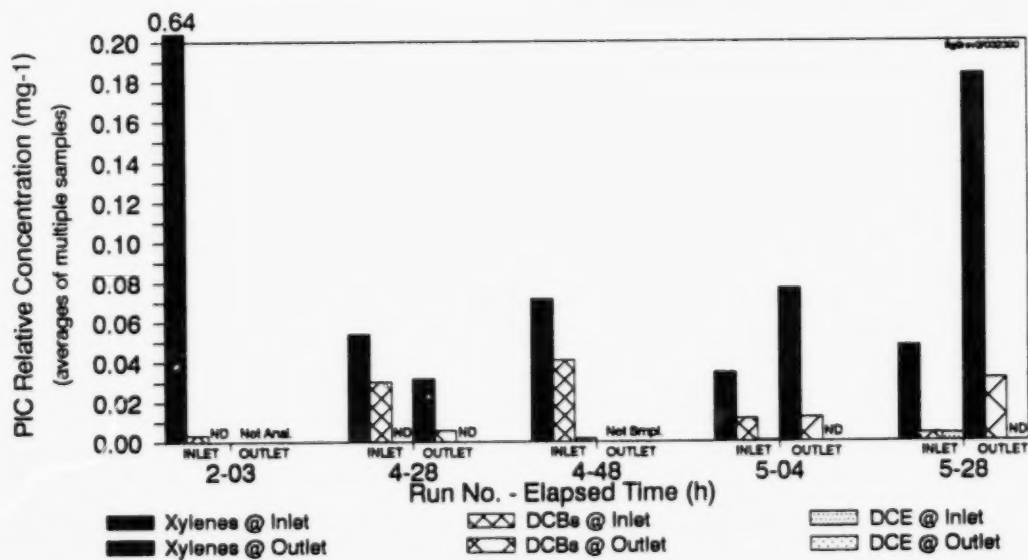


Figure 9. Other PIC results from soot probe samples.

the levels found in Run 4 and Run 5, all of the PICs generally displayed a time-dependent behavior of falling levels at the boiler inlet and rising levels at the boiler outlet. This is similar to what was seen in the POHCs, especially MCB. Of the PICs, toluene showed this hysteresis-type behavior very clearly, whereas the xylenes and naphthalene displayed the effect less clearly than the other PICs. Interestingly, the dichlorobenzenes, which were present at much lower concentrations, also clearly showed the effect.

DCE, which was found only at trace levels, was selected for analysis because it was seen at high stack gas levels. The soot levels are probably low due to the compound's extremely high volatility and related properties.

CONCLUSIONS

At this point, only a limited set of conclusions are offered. Further data evaluation is ongoing, and additional conclusions may be possible in the final project report.

The test successfully accomplished the major objective to evaluate the sorption and desorption of organic compounds on combustion-generated soot during POHC cofiring.

The primary conclusions are:

- The hysteresis effect is real and is measurable under certain conditions.
- Hysteresis can be observed both in the gas phase (stack emissions) and in the solid, sorbent phase (soot).
- The extent of hysteresis is compound-specific, apparently relating to physical and chemical properties such as volatility or molecular size.

The exact impact of the hysteresis effect upon DRE quantitation is not yet known. It appears possible that a DRE could be measurably affected under some conditions, but it also seems likely that the effect would be much less than an order of magnitude. To some extent the degree to which soot is saturated with organics as well as the rates of POHC sorption and desorption will affect DRE measurement. Also, the duration of the trial burn and the duration of waste cofiring which precedes it will be major factors.

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STATE OF THE ART ASSESSMENT
OF MEDICAL WASTE INCINERATION TECHNOLOGY

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ABSTRACT

Incineration is being increasingly utilized as a method for disposing of medical waste since it reduces both the waste's volume and potential hazard. This paper is based upon an ongoing study examining current practices in design and operation of medical waste incinerators with emphasis on identifying incineration process parameters controlling potential toxic emissions. Recent field test results have indicated that medical waste incinerators may be prone to emitting high concentrations of acid gases, toxic organic compounds and other hazardous substances. A variety of incinerator design and operating parameters including chamber temperatures, gas phase mixing, waste feed rate and inclusion of air pollution control devices were found to have important impacts on emissions. It was determined that many of the same mechanisms that are responsible for toxic emissions from municipal and hazardous waste incineration systems are also responsible for emissions from medical waste incinerators. However, medical waste incinerators present unique challenges due to their size and the heterogeneity of the waste.

This paper has been reviewed in accordance with U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Medical waste treatment and disposal is becoming an increasingly important issue. The EPA estimates as much as 14,000 ton/day of medical waste are produced in hospitals in the United States (1). Additional waste is produced in research and diagnostic laboratories, nursing homes, doctors offices and veterinary clinics. Not only is this waste extremely voluminous, but its infectious and sometimes radioactive nature waste requires careful management. The technologies most commonly used to treat medical waste in the United States include steam sterilization, shredding/chemical disinfection, and incineration. Approximately 67 percent of all hospital waste is incinerated on-site. Incineration can provide up to 95 percent waste volume reduction, as well as effectively destroying infectious organisms in the waste. With landfill capacity rapidly diminishing and medical waste generation increasing, incineration is being increasingly viewed as a viable medical waste management technique.

While effective for volume/hazard reduction, incineration of medical wastes presents a unique set of problems. Destruction of hospital wastes by combustion results in formation of air pollutants in solid, liquid, condensible, and gaseous forms. This is one of the most sensitive of air pollution problems, because not only is the general public exposed to these emissions, but the greatest exposure is potentially sustained by that segment of the population which are the least capable of withstanding any further stress to their health: hospital patients.

OBJECTIVES

The objectives of the current study were to define specifically what the most critical emissions problems are and to define the methods currently being used to deal with the problems.

INCINERATION SYSTEMS

There are a wide range of medical waste incineration system types currently in use in the United States. The three most common types are: retort incinerators, modular controlled air systems, and rotary kilns. This paper will focus on these incinerator types. Systems are generally available in either batch or semi-continuous models. Modular controlled air systems are the most commonly manufactured systems in the United States. Figure 1 is a schematic illustration of a modular controlled air incinerator. The primary zone is operated under fuel rich conditions (oxygen deficient) with additional air added at or near the entrance to the secondary chamber. Waste is fed to the primary chamber, usually with a hydraulic ram, allowing the waste to burn on one or more fixed hearths. Small systems typically have only one hearth while larger systems may have 2 or 3 hearths. Small systems, even if they have continuous feed, typically do not provide for continuous ash removal. Such systems are generally designed to operate 8 to 10 hours per day. Large systems typically provide for continuous waste feed and ash removal.

The principal control variables for modern controlled air incinerators are temperatures in the primary and secondary chambers and the volume of those two chambers. Combustion air flow is modulated to maintain primary temperature in the 1400-1600°F range while secondary chamber temperature is controlled typically in the 1800-2000°F range. Auxiliary fuel fired burners are provided to preheat the systems and to assure that secondary chamber temperatures are maintained at regulatory dictated levels. The combination of substoichiometric air addition and large chamber volume in the primary zone create low gas velocities in that region which permit these systems to

achieve low particulate emissions (typically less than 0.1 gr/dSCF) without air pollution control zones. The size of the secondary chambers is established by requirement of local regulations but typically 1 or 2 second residence time is provided in that zone.

POLLUTANT FORMATION

The pollutants of concern are: radioactive materials, pathogens, cytotoxic compounds, toxic metals, trace organics (e.g. PCDD/PCDF) and criteria pollutants (CO, NO_x, SO₂, HCl, PM, PM10).

RADIOACTIVE AND CYTOTOXIC MATERIALS

Radioactive and cytotoxic materials are only a problem when present in the waste. In general, these materials are segregated and disposed of separately.

PATHOGENS

The destruction of pathogens is one of the primary goals of medical waste incineration. There exist some data that indicate that a properly designed and operated incinerator is capable of completely destroying pathogens (2) (3). These data were obtained by spiking the feed with a particular bacteria spore and then testing the residuals and exhaust gases for spore activity. Only in an incinerator operated at very low temperatures, 1100°F, was there found any residual activity. While pathogen destruction is generally complete, an incinerator can be made to operate with poor destruction under abnormal situations. The phenomena likely to affect pathogen destruction include: waste moisture content, uniformity of combustion zone conditions, combustion zone temperature, residence times of solids in the combustion zone including both solids on the bed and particles entrained into the combustion gases, and excess air levels.

TOXIC METALS

Metals are present in large amounts in hospital wastes. Contaminated needles are the most obvious source of metals. However, there are a number of less obvious sources, ranging from the dyes and inks used in printed matter to some pharmaceutical preparations. It is these trace sources of metals which represent the greatest potential danger to human health, for they generally contain the most toxic metals.

In Table 1 are data from a hospital waste incinerator in California (4). This study indicated that the fly ash was highly enriched relative to the bottom ash with lead, cadmium, chromium and arsenic. Even when equipped with a baghouse, emission of cadmium and lead were found to be relatively high. Because medical waste incinerators are small, these emissions may not significantly increase the metals concentrations in the atmosphere. However, multipathway risk analyses performed by California Air Resource Board indicate that the incremental lifetime cancer risk associated with the cadmium emissions from medical waste incinerators can be as high as 500 chances in a million (5).

A number of mechanisms control the behavior of metals during the incineration of hospital wastes. These mechanisms can be identified by examining data available from a variety of incineration systems and are discussed in detail by Barton et al. (6). The key phenomena, illustrated in Figure 2, are vaporization and subsequent condensation of volatile metals,

entrainment of metals bearing solids, and reactions between metals and other elements (esp. Cl). New insight into the importance of these mechanisms has been obtained from recent tests of hazardous waste incinerators (7) (8).

The important hospital waste incinerator operating parameters that influence metals emissions can be identified using field data and an understanding of the controlling mechanisms. The most important parameter is, of course, the amount and type of metals in the waste. As previously discussed, the metals that are volatile at combustion conditions or are converted to volatile form such as As, Cd, Pb and Hg are particularly difficult to control. Other system parameters expected to influence metal emissions include the following: the maximum temperatures of solids in the primary zone, chlorine content of waste since chlorides of metals such as lead tetrachloride can form salts which are extremely volatile, primary zone gas velocity which dictates particle entrainment, the temperature of the particle control device since this determines how much of the volatile metals have recondensed and can therefore be captured, and the fine particle control of the APCD and parameters such as pressure drop which influence the control levels.

CHLORINATED DIOXIN/FURANS

One of the greatest challenges that remains for the disposal of medical waste by incineration is the control of emissions of trace organics such as polychlorinated dibenzo(p)dioxin and furans (PCDD/PCDF). There have now been several studies which have indicated that medical waste incinerators can generate relatively high levels of PCDD/PCDF. In Table 2 are provided data from a wide variety of combustion sources, including three medical waste incinerators. These data have an average total PCDD/PCDF level of approximately 700 ng/Nm³. This compares to large modern mass burn municipal waste incinerators such as Marion, Tulsa, and Wurzburg which have average total PCDD/PCDF levels of less than 30 ng/Nm³ and hazardous waste incinerators which can range from 25 to 3000 ng/Nm³.

Figure 3 illustrates the various potential mechanisms that have been proposed for formation of PCDD/PCDF in incinerators. One of the simplest mechanisms is that the emitted dioxins were originally present in the waste and were not destroyed in the incinerator. While this mechanism may be responsible for a very small fraction of the emitted PCDD/PCDF most wastes do not contain sufficient quantities of PCDD/PCDF to account for the observed emission levels.

In the second potential mechanism, dioxins are formed as intermediates in the oxidation of more complex hydrocarbons. The hydrocarbons may be chlorinated (PVC for example) or not (cellulose). If the dioxins are originally unchlorinated the chlorination must take place as a second step.

The third potential dioxin formation mechanism involves reactions between relatively simple gas phase precursors such as phenols and chlorobenzenes. Shaub and Tsang (9) developed a kinetic model to study the characteristics of the proposed reactions. Ballschmitter et al. (10) and Benenfinati et al. (11) examined the emissions from full scale incinerators and found a close relationship between the dioxin emissions and the quantity of polychlorobiphenol and polychlorophenol in the exhaust. They suggested that this indicates that dioxins are formed by reactions involving PCBs and PCPs.

The final mechanism that has been proposed calls for fly ash catalyzed formation of dioxins in relatively cool regions of the incinerator. This last mechanism was originally proposed by Vogg and Stieglitz (12) and is supported by laboratory experiments. Extensive experiments are under way in Germany, Canada and the U.S. to extend Vogg and Stieglitz's work on full-scale

systems. Limited results available to date indicate that PCDD/PCDF emissions are closely related to the quantity of entrained particles and the amount of gas phase hydrocarbons (13).

Based on the mechanisms described above, it can be hypothesized that PCDD/PCDF formation can be minimized by controlling particle emission levels within the incinerator, minimizing the time particles are held at key temperatures (between 480°F and 666°F) and by maximizing the destruction of precursors both vapor and particle bound within the incinerator. Also dioxins can ultimately be removed from the flue gas through the use of fine particle control since PCDD/PCDF will condense on particles at low temperatures.

CRITERIA POLLUTANTS

The incineration of medical wastes can generate a variety of acid gases such as SO_2 , SO_3 , NO_x , HCl and HF . NO_x can be formed by oxidation of the nitrogen in air and in the wastes. The other gases are typically formed by the chemical reaction of sulfur, chlorine and other elements in the waste. The most common occurrence is the formation of HCl , and thus in most hospital waste incinerators, HCl is the principal acid gas of interest. During combustion, the organic chloride in the waste reacts with hydrogen to form hydrogen chloride, HCl . The organic chloride can be found in many substances commonly burned in hospital waste incinerators including plastic bags, disposable syringes and plastic tubing. It is possible for free chlorine to form when the combustion chamber contains an insufficient quantity of hydrogen to convert all of the organic chlorine to HCl , but this is very uncommon.

AIR POLLUTION CONTROL DEVICES

Until very recently medical waste incinerators were typically not equipped with air pollution control devices. Prevailing particulate emissions standards could be achieved without APCDs; CO emission levels were generally below 25 ppm and acid gas from small sources were not a major concern for local regulators. However, that situation is changing drastically. New York, for example, is requiring that APCDs be retrofit to all existing medical waste incinerators. While many types of advanced APCDs are available (e.g. wet electrostatic precipitators and ionizing wet scrubbers) two types of add-on APCD are receiving major attention. These are illustrated in Figures 4 and 5 and include (1) a venturi scrubber followed by a packed tower and (2) duct injection of a calcium based sorbent followed by a fabric filter. The venturi scrubber achieves particulate capture largely by impacting the particles with water droplets. The venturi configuration is used to provide a high relative velocity between the particles and water. Increased relative velocity increases impaction and particulate capture but is achieved at the expense of high pressure drop. Modern, venturi scrubbers provide 30 to 40 inches W.G. to achieve exit particulate loadings on the order of 0.03 gr/dSCF. Since HCl and SO_2 are highly soluble in water the combination of water sprays in the venturi and in the packed tower are extremely effective in removing acid gases. Typically, caustic is added to keep the scrubber liquid pH in the 6.5 to 7.0 range. Total acid gas removal efficiency on the order of 98 to 99 percent is routinely achieved.

Duct injection followed by fabric filtration is currently finding increased popularity--particularly among regulators who have based rules for medical waste incinerators on municipal waste combustion experience. As with municipal waste combustion applications the fabric filter is able to achieve particulate loading on the order of 0.015 gr/dSCF with pressure drops on the order of 10 inches W.G. This system does not drop the flue gas temperature below the dew point and must achieve acid gas capture with injected sorbent. Using about 2:1 stoichiometric calcium to acid gas molar ratios, about 90 percent acid gas control is achievable.

SUMMARY

The pollutants of principal concern from medical waste incinerators include: volatile metals such as As, Pb, Cd, Hg; highly toxic materials such as: PCDD/PCDF and hexavalent chromium; HCl; and fine particles (PM10). In the case of HCl, the waste chlorine level and the performance of any air pollution control device scrubbers are dominant. Waste chlorine levels are highly variable and not easily quantified. Thus the focus comes back to the proving that the scrubber efficiency is sufficient to control any levels of HCl emissions. Since even short-term exposures to HCl are a measurable risk, the short-term control efficiency must be determined.

For toxic metals, the volatile species such as arsenic, lead and cadmium are of principal concern because they escape the incinerator as a vapor and condense into an ultrafine fume that is not easily captured and is highly respirable. However, some metals are carcinogenic and even low emission levels are important. Again, the amount of these metals present in the hospital waste is, of course, the dominant variable for control of their emission. However, it is virtually impossible to either quantify the metals in the input waste stream or to control the levels due to the trace quantities of concern and the ubiquitous nature of many of the metals such as chromium and lead. The key operating parameters are those that control the volatilization of metals (such as temperature, excess air and chlorine levels) and those that control fine particulate capture.

Finally, the emissions of PCDD/PCDF are expected to be the result of a complicated interrelationship between waste properties, combustion conditions, and scrubber/fine particulate control. The primary control parameters were identified as - combustion uniformity, combustion zone mean temperature, fine particle control efficiency, APCD temperature, and particle loading exiting furnace (determined by incinerator load, velocities and waste properties).

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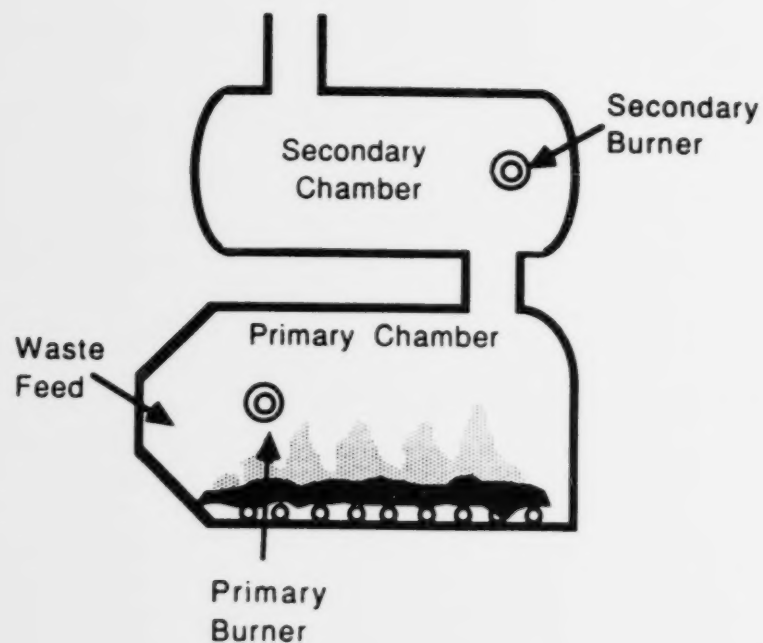


Figure 1. Typical modular starved incinerator.

TABLE 1. METALS EMISSIONS FROM CEDARS-SINAI MEDICAL CENTER INCINERATOR

METAL	BAGHOUSE ($\mu\text{g/gm}$)	BAGHOUSE CATCH ($\mu\text{g/gm}$)	BOTTOM ASH ($\mu\text{g/gm}$)
LEAD	18051	89	1700
IRON	2401	3100	17400
MANGANESE	175	240	230
NICKEL	30.7	33	33
CADMIUM	1792	1700	2.8
CHROMIUM	78	1	0.7
ARSENIC	86	4.7	0.7

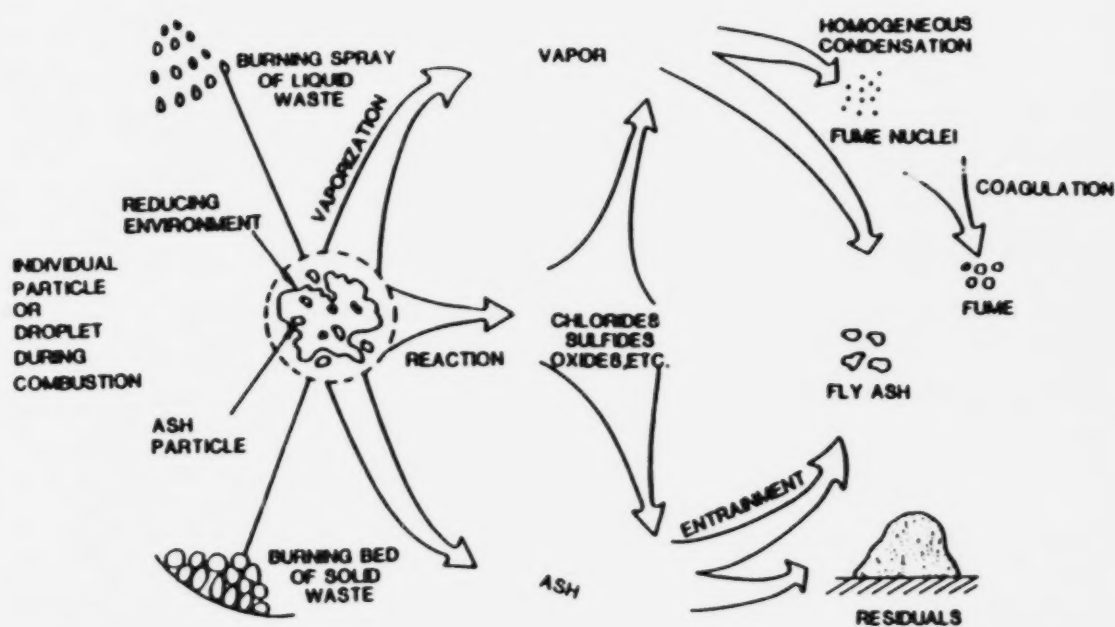


Figure 2. Phenomena affecting metals behavior during incineration.

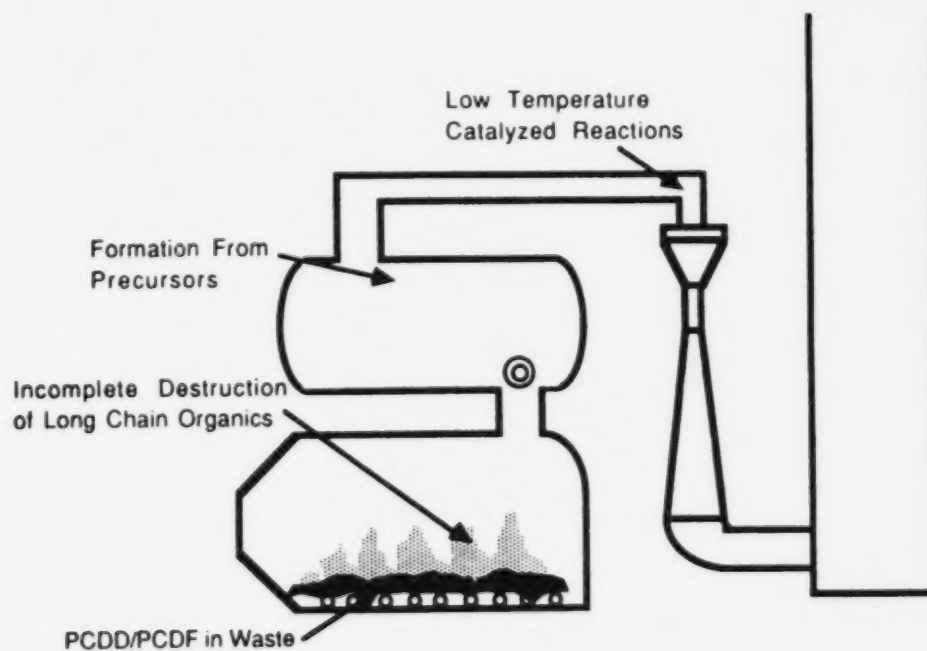


Figure 3. Potential PCDD/PCDF formation mechanisms.

TABLE 2. PCDD/PCDF EMISSIONS SUMMARY

	ug/Mg	PCDD ng/Nm ³	ug/Mg	PCDF ng/Nm ³
<u>Hospital Waste</u>				
Cedar Sinai	1988	160-260	5384	386-700
Saint Agnes	6272	290-450	10961	700-785
Royal Jubilee	1625-2680	117-197	715-1115	52-84
<u>Hazardous Waste</u>				
Hazardous Waste Incinerators		20 - 600		5 - 2400
<u>Municipal Waste</u>				
Hampton	1000-27000	243-10700	1770-41200	400-37500
North Andover		225		323
Marion Co.	5.2	1.13	1.9	
Prince Edward Island	200-500	60-125	300-500	100-160
Tulsa	74.5	18.9	61.1	15.5
Wurzburg	62.7	22.1	79.2	27.9
Akron	636	258	1680	679
<u>Tier IV</u>				
Black Liquor		2-17		1.5-45
Wood Fired Boiler		102		154
Carbon Reg Furnace		28.8		70.1
Sewage Sludge		114		507
Drum & Barrel Reclamation		687		2107

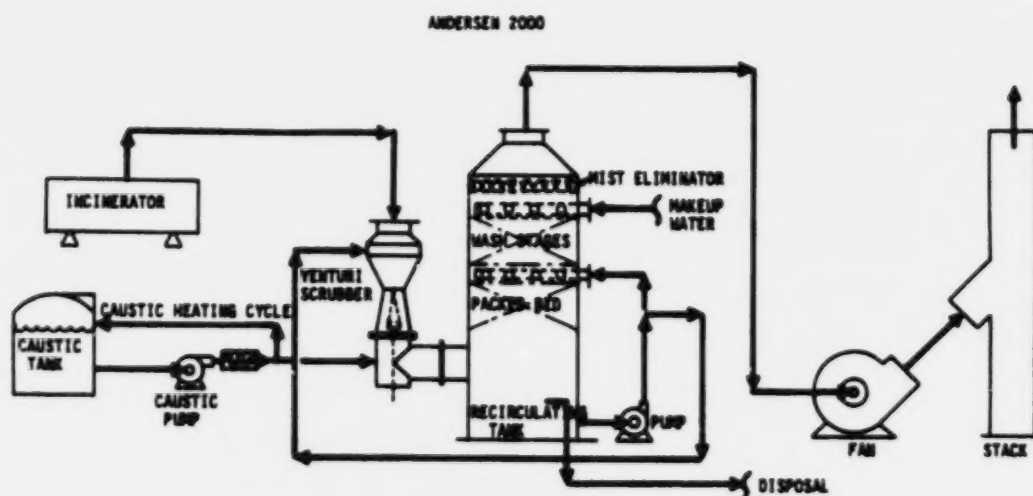


Figure 4. Schematic of wet venturi scrubber and packed tower for application to medical waste incinerators.

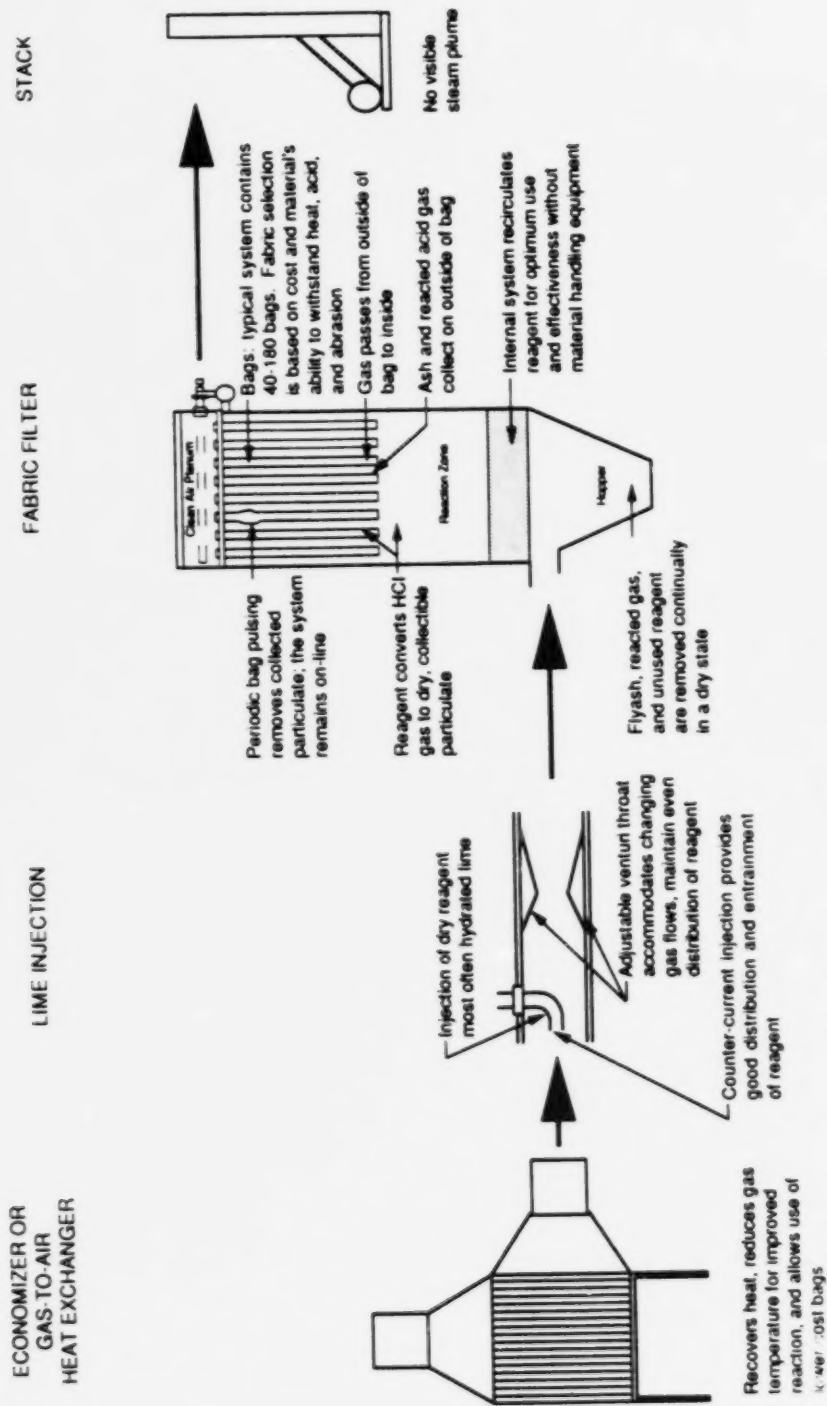


Figure 5. Schematic of duct injection fabric filter APCD for application to medical waste incinerators.

THE INCINERATION OF ARSENIC-CONTAMINATED SOILS
RELATED TO THE COMPREHENSIVE ENVIRONMENTAL RESPONSE,
COMPENSATION AND LIABILITY ACT (CERCLA)

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ABSTRACT

The thermal fate of arsenic in CERCLA soils has been evaluated at the USEPA Incineration Research Facility at Jefferson, Arkansas. This facility houses a pilot-scale rotary kiln incinerator which was fed an arsenic-contaminated soil for the reported study. The analytical results indicate that as much as 75 percent of the measured arsenic fed to the kiln was contained in the kiln ash; about 20 percent was removed by the air pollution abatement system; and the other 5 percent was found in the particulate emissions. Preliminary muffle furnace tests completed on the same soils indicated that both the volatility and leachability of arsenic were reduced when lime was added to the arsenic-containing soil before thermal treatment.

INTRODUCTION

The Incineration Research Facility (IRF) at Jefferson, Arkansas, has, as a primary mission, the support of the Environmental Protection Agency (EPA) Regional Offices and the Office of Solid Waste and Emergency Response in evaluation of incineration as a disposal option for wastes which are undergoing remedial actions at Superfund sites. A priority site in Region I is the Baird & McGuire location in Holbrook, Massachusetts. EPA Region I requested test burns of contaminated soil from this location to support the evaluation of the suitability of incineration as a treatment technology for remediation of this Superfund site. The soil contained the principal metals arsenic and lead and a wide variety of pesticides (pp'-DDT, pp'-DDD and pp'-DDE and Methoxychlor). Incineration was proposed to destroy the organics, but the fate of arsenic (or metals) was of concern. The principal mission of the test was to evaluate the incinerator operating conditions, and how they would impact the partitioning of the arsenic to the various residual streams. The purpose of this presentation is to identify the arsenic content of the discharge streams: ash, scrubber water and atmospheric emissions.

EQUIPMENT

The experimental work was conducted at the USEPA Incineration Research Facility (1). The rotary kiln incineration system (RKS) was used for this research. The design characteristics of the kiln system are:

Main Chamber

Length, outside	2.61 m (8 ft - 7 in.)
Diameter, outside	1.22 m (4 ft)
Length, inside	2.44 m (8 ft)
Diameter, inside	0.95 m (3 ft - 1-1/2 in.)
Chamber volume	1.74 m ³ (61.4 ft ³)
Construction	0.63 cm (0.25 in.) thick cold-rolled steel.
Refractory	12.7 cm (5 in.) thick high alumina castable refractory, variable depth to produce a frustroconical effect for moving solids.
Rotation	Clockwise or counterclockwise 0.2 to 1.5 rpm
Solids retention time	1 hr (at 0.2 rpm)
Burner	North American Burner, rated at 770 kW (2.6 MMBtu/hr) with liquid feed capability.
Primary fuel	Natural Gas
Feed System	
Liquids	Positive displacement pump via water-cooled lance.
Sludges	Moyno pump via front face, water-cooled lance.
Solids	Metered twin-auger screw feeder or fiber pack ram feeder.
Temperature (max)	1010°C (1850°F)

Characteristics of the Afterburner Chamber

Length, outside	3.05 m (10 ft)
Diameter, outside	1.22 m (4 ft)
Length, inside	2.74 m (9 ft)
Diameter, inside	0.91 m (3 ft)
Chamber volume	1.80 m ³ (63.6 ft ³)
Construction	0.63 cm (0.25 in.) thick cold rolled steel
Refractory	15.24 cm (6 in.) thick alumina castable refractory
Gas residence time	1.2 to 2.5 sec depending on temperature and excess air
Burner	North American burner rated at 590 kW (2.0 MMBtu/hr) with liquid feed capability
Primary fuel	Natural gas
Temperature	1200°C (2200°F)

Characteristics of the Ionizing Wet Scrubber APCD

System capacity	85 m ³ /min (3000 acfm) at 78°C (172°F) and 101 kPa
inlet gas flow	(14.7 psia)
Pressure drop	1.5 kPa (6 in. wc)
Liquid flow	15.1 L/min (4 gpm) at 345 kPa (50 psig)
pH control	Feedback control by NaOH solution addition

EXPERIMENTAL TEST PROGRAM

MUFFLE FURNACE EXPERIMENTATION

A series of waste composition/leachability tests was conducted in a muffle furnace prior to incinerator testing to determine the optimum experimental conditions. The muffle furnace tests consisted of 9 experiments during which various concentrations of arsenic in the contaminated soil were heated at 982°C (1800°F) for 1 hour. The weight losses (moisture and volatiles) were determined for each sample, and the resulting ash was analyzed for total arsenic (As). Clay was mixed with the soil to get variable arsenic concentrations in the feed. Toxicity Characteristic Leaching Procedure (TCLP) leachates of the feed as well as the ash were also taken and analyzed for arsenic and compared with the total waste/ash analysis. Two percent lime by weight was added to one of the samples and two percent alum (ferric ammonium sulfate, $\text{FeNH}_4(\text{SO}_4)_2$) was added to another of the samples.

INCINERATOR TESTING

A series of five (5) tests was performed using the RKS at the IRF to determine the relative partitioning of arsenic to the different waste streams. These were a part of the testing series to establish that incineration effectively destroyed the organic contaminants in the soil and to evaluate the fate of arsenic and lead as a function of incineration conditions.

The incineration condition test variables were kiln temperature and kiln air flow. Kiln temperature was targeted for 816 and 982°C (1500 and 1800°F), and the air flow from the kiln exit flue was targeted at 6 and 10 percent oxygen.

All the soil was fed to the kiln in fiber-pack drums via the RKS ram feeder system. The fiber-packs, each of which contained about 5.0 kg (11 lb) of soil, were fed at the rate of one every 5 minutes. The kiln rotation was set to give a nominal solids residence time of 0.5 hr.

SAMPLES

The samples taken during each test were:

1. Scrubber blowdown water for arsenic,
2. Feed and kiln ash for total arsenic analysis,
3. O_2 concentrations at kiln outlet,
4. Stack gas for arsenic incorporated into the particulate matter and POHCs, and
5. Feed and ash for TCLP determinations.

TEST RESULTS AND DISCUSSION

MUFFLE FURNACE TEST RESULTS

Soils with varying concentrations of arsenic were heated in the muffle furnace to determine the effect of arsenic feed concentration on the resultant arsenic ash concentration and leachability. TCLP leachates of the feeds and ashes were analyzed for arsenic to observe the effects on arsenic mobility.

The test results are summarized in Table 1. These data show the various concentrations of arsenic which were derived by mixing the contaminated soil, which contained 655 mg/kg of arsenic, with uncontaminated clay.

These data from muffle furnace tests suggest that an initial arsenic concentration of about 200 mg/kg would be the maximum feed contamination level which can be incinerated if the TCLP guidance level of 5 mg/L for the ash is to be maintained. It may be possible to increase the partitioning of arsenic to the ash and maintain low TCLP values if lime was added to the material before it was incinerated.

The addition of 2 percent lime by weight to 100 percent of the contaminated soil increased the arsenic retention in the ash to 83 percent. The addition of the lime reduced the TCLP value by 53 percent when compared to an untreated sample.

The addition of 2 percent alum had the opposite effect on the arsenic retention in the ash with the retention being reduced to 38 percent. The TCLP was 9.8 mg/L as compared with 6.5 mg/L when lime was added indicating that the retaining properties of alum were less than lime. Figure 1 shows the TCLP values determined for each soil concentration and the resulting ash TCLP for the data shown in Table 1. The soil that was processed had a consistently higher TCLP value than its corresponding untreated soil.

INCINERATION TEST RESULTS

Five incineration tests were conducted at the IRF on a contaminated soil (at the arsenic concentration as received) from the Baird & McGuire site. Table 2 summarizes the resulting distribution of arsenic in the ash, kiln exit gases and scrubber water. The ash generation rate was determined by using the feed rate, less the volatiles and moisture.

The test results are contained in Table 2. Table 2 is the arsenic material balance and a general summary. This table has been arranged by temperatures of operation, so the Tests 1, 2 and 5 are the 816°C (1500°F) condition, and Tests 3 and 4 are the 982°C (1800°F) operating condition. Test 5 was a duplicate of Test 2 to check the data precision.

Table 2 shows the conditions of operation. Tests 1, 2 and 5 had target temperatures of 816°C (1500°F). The mean experimental temperatures achieved were 832°C (1530°F), 839°C (1540°F) and 844°C (1551°F). Tests 3 and 4 had a

target temperature of 982°C (1800°F) and operated at 994°C (1821°F) for both tests. Temperatures for all tests were close to the target conditions and judged successful. For ease of presentation, the temperatures 816°C (1500°F) will be used for Tests 1, 2 and 5, and 982°C (1800°F) will be used for Tests 3 and 4. The actual temperatures achieved are used in the table.

For the same reasons discussed above, the oxygen concentrations of 7 percent and 11 percent are used in the text presentation. Tests 1, 3 and 5 were at the 11 percent concentration and Tests 2 and 4 were at the 7 percent concentration. Operating the kiln at 816°C (1500°F) resulted in the lower arsenic emissions at the stack. At the 11 percent kiln oxygen rate (high air flow rate), the arsenic emissions at the stack were 4.3 and 3.6 percent of the feed for Tests 1 and 5. For Test 3, at the 11 percent oxygen and 982°C (1900°F) kiln operating temperature, the emissions of arsenic at the stack were 5.5 percent of the feed. Using the lower temperature reduced the arsenic emissions at the stack over 35 percent.

The lower oxygen concentration (7 percent) (lower air flow rate) at the kiln outlet further reduced arsenic emissions to the atmosphere. At 816°C (1500°F) and 7 percent oxygen at the kiln, the emissions were 2.1 percent of the feed compared to 4.7 percent at 982°C (1800°F). The 982°C (1800°F) had an emission rate of arsenic over 100 percent higher than the 816°C (1500°F) operating at the lower air flow.

Incinerating the soil at 816°C (1500°F) and 7 percent oxygen at the kiln outlet (low air flow) was the best operating condition of the five tests for limiting arsenic stack emissions. The retention of ash in the feed was 85 percent of the arsenic feed and the emissions to the atmosphere were 2.1 percent of the arsenic feed. Operating at the lower kiln temperature of 816°C (1500°F) and the lower oxygen concentration, lower air flow increased the retention of arsenic in the ash and reduced the emissions to the atmosphere. The retention of arsenic in the ash was 84.6 percent at 816°C (1500°F) and 6.8 percent oxygen.

The lowest retention of arsenic in the ash was 29.8 percent at 982°C (1800°F) operating temperature, and elevated oxygen concentrations. Ash retention data reinforces the emissions data at the lower air flow and lower temperature of operation.

The ash from the RKS tests had a greater TCLP value than the feed in all cases (Table 3). It was suggested that the incineration of the contaminated soil destroyed the part of the soil matrix that was holding the arsenic. Once incinerated, the arsenic became much more mobile and produced higher TCLP values. Based on drinking water health effects data, the guidance TCLP for arsenic is 5 mg/L, and the highest ash TCLP value from these tests was 1.24 mg/L. Therefore the TCLP of the ash was well below guidance values for all tests.

The data reported in this paper are in line with full scale emissions data previously obtained on arsenic. Gerstle (2), in analysis of metals data from sewage sludge incinerators found that an increase in temperature from 1300°F to 1500°F would double the emissions of arsenic. An additional

increase in temperature to 1700°F would quadruple those experienced at 1300°F. Higher temperatures for incineration require more oxygen (air flow), thus more air flow resulting in a more turbulent combustion zone. The turbulent conditions will entrain more particulate. A reduction of O₂ at the kiln outlet for the RKS may be equivalent to Gerstle's reduction in temperature. If the RKS behaved thermally in the same manner as the sludge incinerator, the average expected arsenic emission would be 0.8 to 2 percent of the feed at 1500°F and would be 20 to 100 percent at 1800°F. The question of comparability notwithstanding, the RKS appears to have done much better in partitioning the arsenic to the ash.

CONCLUSIONS

1. Of the operating conditions tested, the largest percentage (85 percent) of arsenic retained in the ash was at 816°C (1500°F) and 7.5 percent oxygen.
2. Operating conditions at the lower temperature 816°C vs. 982°C (1500°F vs. 1800°F), increased arsenic retention in the ash.
3. Reduced oxygen rates (air flow rates) gave increased retention of the arsenic regardless of the operating temperature.
4. Reduced oxygen rates (air flow rates) decreased emissions at the stack outlet.
5. The TCLP of the ash in these tests was always lower than the 5 mg/L guidance limits.

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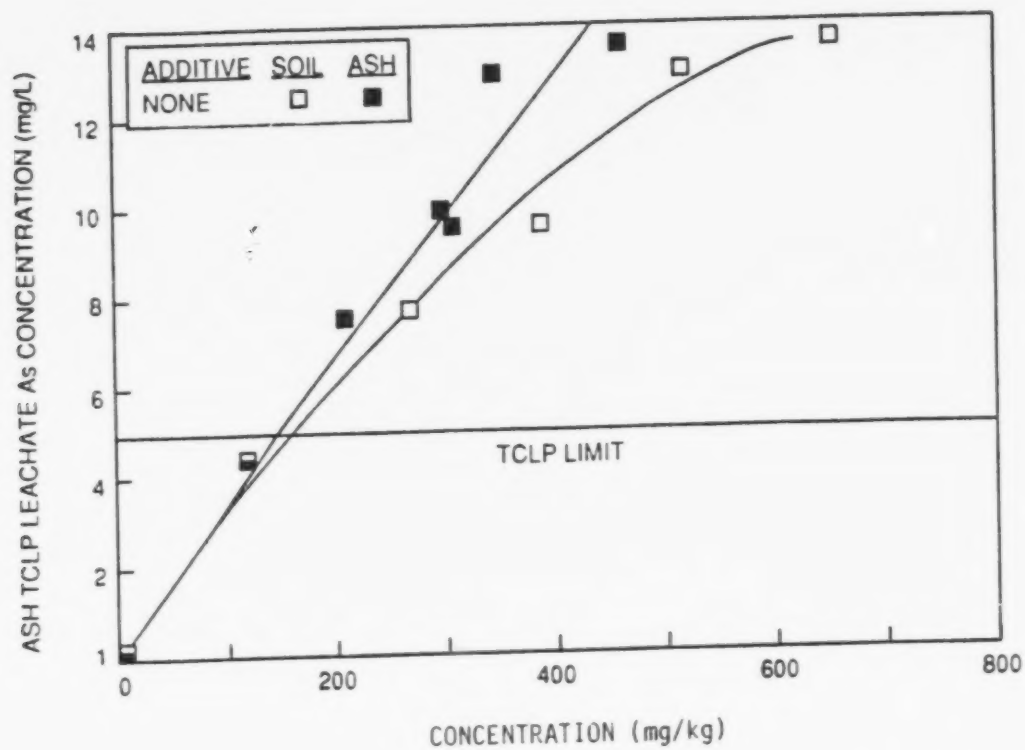


Figure 1. TCLP leachate, mg/L, vs. arsenic concentration in soil and in resulting ash from muffle furnace.

Table 1. Muffle Furnace Results

Concentration of arsenic in soil mg/Kg	Expected ash arsenic concentration (dry basis)* mg/Kg	Measured ash concentration arsenic mg/Kg	Fraction remaining in ash (percent)	TCLP ash mg/L
655	863	468	54	13.7
524	701	351	50	13.0
339	528	310	59	9.4
328	437	299	68	9.8
262	351	211	60	7.6
131	174	130	75	4.5
<5	<7	5.1	-	<0.07
642 ⁺	862	716	83	6.5
642 [#]	879	330	38	9.8

*dry basis calculated using moisture and volatile removal

⁺2% lime added

[#]2% alum added

Table 2. Incinerator Test Results

Test No.	Incinerator kiln temp. ^o	Arsenic % Oxygen content of flue gas at kiln exit	Arsenic retention in ash, % of feed mass	in scrubber water* % of feed	Arsenic in the stack gas	Metal balance % of feed
1	832	11	71.9	19	4.3	95
5	839	11	57.2	21	3.6	82
2	844	6.8	84.6	22	2.1	109
3	994	10.4	29.8	34	5.5	69
4	994	7.5	41.9	30	4.7	76

*scrubber water and stack emissions

Table 3. Summary of Test Results

Test No.	Temp °C	Arsenic in feed rate mg/kg	Arsenic retained in ash % of feed	Arsenic emitted at stack ratio to feed mass g/kg	Arsenic TCLP of ash mg/L	Arsenic TCLP of feed mg/L
1	832	82.2	71.9	.0035	0.3	0.1
5	839	82.8	57.2	.0031	0.2	0.1
2	844	92.6	84.6	.0081	1.2	0.1
3	994	80.5	29.8	.0051	0.2	0.1
4	994	83.5	41.9	.0038	1.2	0.1

FUNDAMENTAL STUDIES ON PARTICULATE EMISSIONS
FROM HAZARDOUS WASTE INCINERATORS

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ABSTRACT

A fundamental study has been carried out to understand the formation and growth of metallic particles in incinerators. A bench scale flame incinerator was used to perform controlled experiments with lead acetate and silicon tetrachloride as the test compounds. A dilution probe and real time aerosol instruments were used to measure the particle size distributions at different locations in the flame region. A lognormal aerosol model accounting for particle formation by nucleation and chemical reaction, and growth by condensation and coagulation was used to predict the evolution of the particle size distribution. Reasonable agreement was obtained between the model predictions and experimental results in view of the limitation of the aerosol measuring instruments. Condensation was the dominant growth mechanism for the lead aerosol. With silicon tetrachloride as the test compound, non-volatile silica particles were formed, and coagulation was the dominant mechanism of particle growth.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. The conclusions represent the views of the authors and do not necessarily represent the opinions, policies, or recommendations of the U.S. Environmental Protection Agency.

INTRODUCTION

Emissions from hazardous waste incinerators are currently regulated by the Resource Conservation and Recovery Act (RCRA) incinerator performance standards (1). The requirements of 99.99 % destruction and removal efficiency for each principal organic hazardous constituent (POHC), and 99 % removal of the HCl gas have been met in most cases of hazardous waste incinerator operation. However, the particulate emission standard of 180 mg/m³ has often been violated (2). Combustion processes are the major sources of toxic metal loadings in the atmosphere, with waste incineration and coal combustion being the two major contributors (3). Waste incinerators are becoming popular as they lead to significant reduction in volume of the original waste (90 to 95 % by volume). However, stack gas emissions from these units, especially those of toxic volatile metals, are of great concern. Vogg et al. (4) report enrichment factors of 20 for Pb, 60 for Sb, 100 for Cd, and 600 for Hg during waste incineration. It has been well recognized that the submicron particles are enriched with volatile metals such as Hg, Pb, Cd, As, and Zn.

Many studies have been conducted to examine particulate emissions from incinerators in operation. Very few have examined detailed size distributions of these particulate emissions, especially in the submicron range. These submicron sized particles are collected with lowest efficiency in the control devices, and are the most harmful to human health (4, 5). A notable exception is the work by Kauppinen and Pakkanen (5) who reported aerosol size distributions from hospital refuse incineration. The submicron sized particles were significantly enriched with toxic elements like Pb and Cd.

If incineration is to be an effective alternative to conventional hazardous waste disposal methods, there is need for a better understanding of toxic particle formation processes in such systems. In order to effectively design and choose particle control devices for such incinerators, it is imperative that the particle size distributions of the emissions be known. A model to predict formation and growth of volatile particles in a flame incinerator system has been developed by Sethi and Biswas (6). This paper describes a bench scale experimental system to perform studies to verify the predictions of the model.

EXPERIMENTAL SYSTEM

The schematic of the experimental system to study the evolution of the

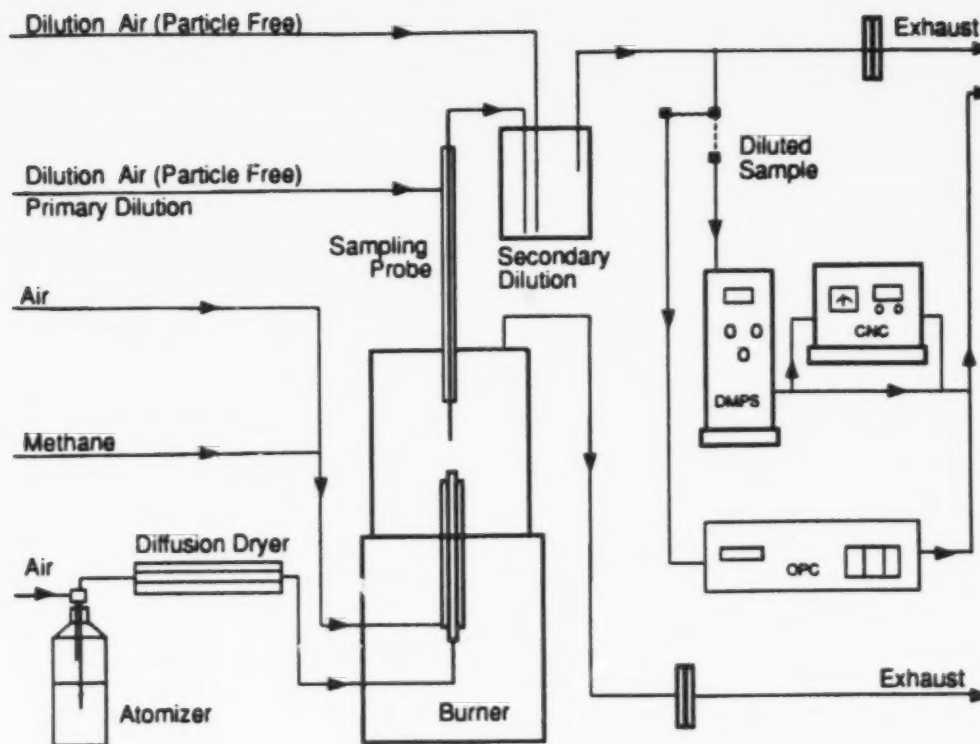


Figure 1. Schematic diagram of the experimental set-up.

particle size distribution is shown in Figure 1. It consists of a methane/air laminar flow burner. The test compound is introduced into the flame region through one of the ports of the burner. Experiments were performed using lead acetate and silicon tetrachloride. In the case of Pb, an aqueous solution of lead acetate was atomized, diffusion-dried, and introduced into the flame as an aerosol. Silicon tetrachloride, for the other case, was introduced into the flame as a vapor entrained in Ar as the carrier gas passed through a bubbler. A dilution probe was used to draw out samples from the flame for size distribution measurements in real time (7). Particle free air was used as a dilution gas to freeze all chemical reactions and aerosol dynamic effects once the aerosol enters the probe. A secondary dilution system using particle free air was used to ensure that the concentrations were lower than 10^6 particles/cm³ to be within the instrument measuring range. A Differential Mobility Particle Sizer (DMPS; manufactured by TSI, Inc.) was used to measure the particle size distributions for the silica tetrachloride feed tests and an Optical Particle Counter (OPC; manufactured by PMS, Inc.) was used for the Pb aerosol feed tests. The gas

was passed through a filter before being exhausted into the hood. The experimental conditions are listed in Table I.

TABLE I. EXPERIMENTAL CONDITIONS

FLAME CHARACTERISTICS:	
Methane Flow Rate, lpm	1.0
Air Flow Rate, lpm	2.5
Burner Diameter, cm	0.2
LEAD COMPOUND:	
Solution Concentration, g/cm ³ lead acetate in Atomizer	0.159
Feed Aerosol Concentration, 10 ⁵ #/cm ³	5.0
Feed Aerosol Volume Average Diameter, μ m	0.5
Feed Aerosol Geometric Standard Deviation	1.4
SILICON COMPOUND:	
SiCl ₄ Feed Rate, mg/min	20
Carrier Gas	Ar

RESULTS AND DISCUSSION

The temperature history in the flame is important as it determines the rate of different physico-chemical phenomena. The experimentally determined temperature profile as a function of distance from the burner inlet as measured by a very fine wire 'R' type thermocouple is shown in Figure 2. The solid line in Figure 2 is a prediction of the temperature profile (6). Reasonable agreement is obtained between model predictions and measured data; the trend and peak values are in good agreement. The differences close to the burner inlet are because the model assumes the flame to be a pure diffusion flame and neglects radiative heat transfer with the surroundings.

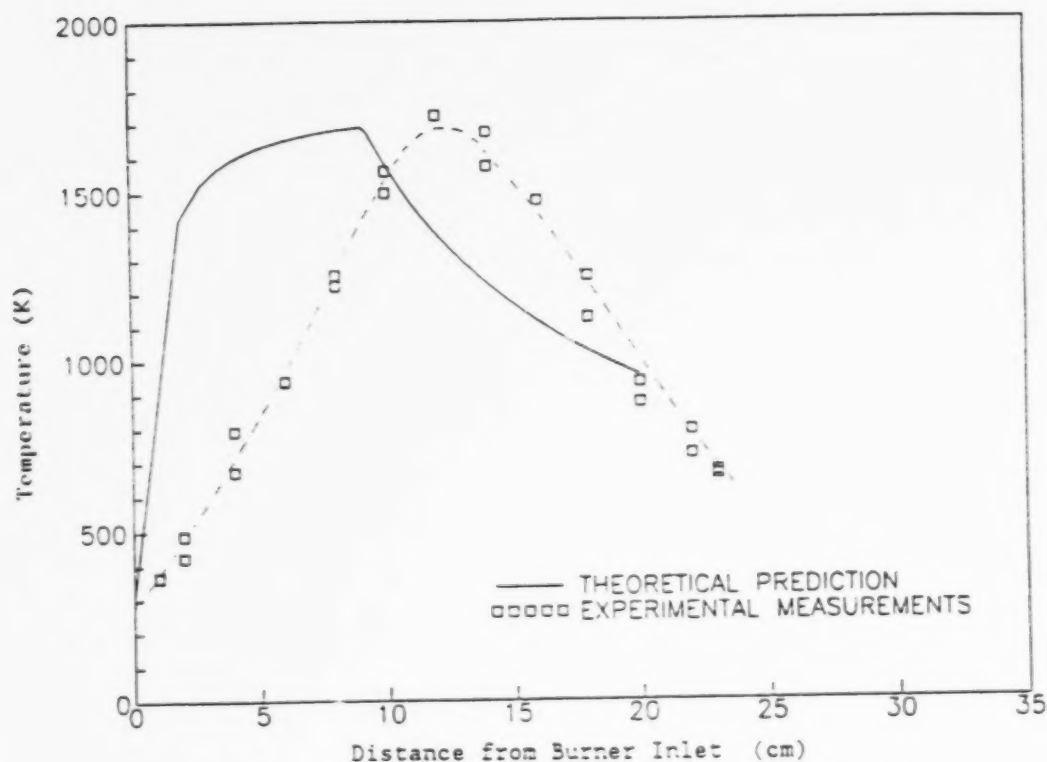


Figure 2. Comparison of the theoretical and experimental flame temperature profiles.

Experiments were conducted with lead acetate aerosol and the results are plotted in Figure 3. The experiments were repeated three times for the same inlet conditions and the evolution of the average volume concentration, number concentration, volumetric mean particle size, and geometric standard deviation is plotted in Figures 3(a), (b), (c), and (d), respectively. The vertical bars in the figures represent variability in the data while repeating the experiments. As the Pb compound enters the flame, the particles tend to evaporate in the high temperature region of the flame, and there is a steep decrease in both the aerosol number and volume concentration (0 to 10 cm). Predictions from the theoretical model indicate that the Pb will be completely in the vapor state in the flame region (6). On proceeding downstream of the flame, the temperature decreases (Figure 2); therefore, the saturation ratio of the Pb vapor increases. This vapor then nucleates into fine particles, and there is an increase in both number and volume concentration, as the vapor is now converted to the particle phase where further growth takes place by condensation and coagulation. The experimental data reflect a similar trend. The measured number concentrations are low in the high temperature regions of the flame zone (3 to 10 cm) and essentially reflect complete evaporation of the Pb

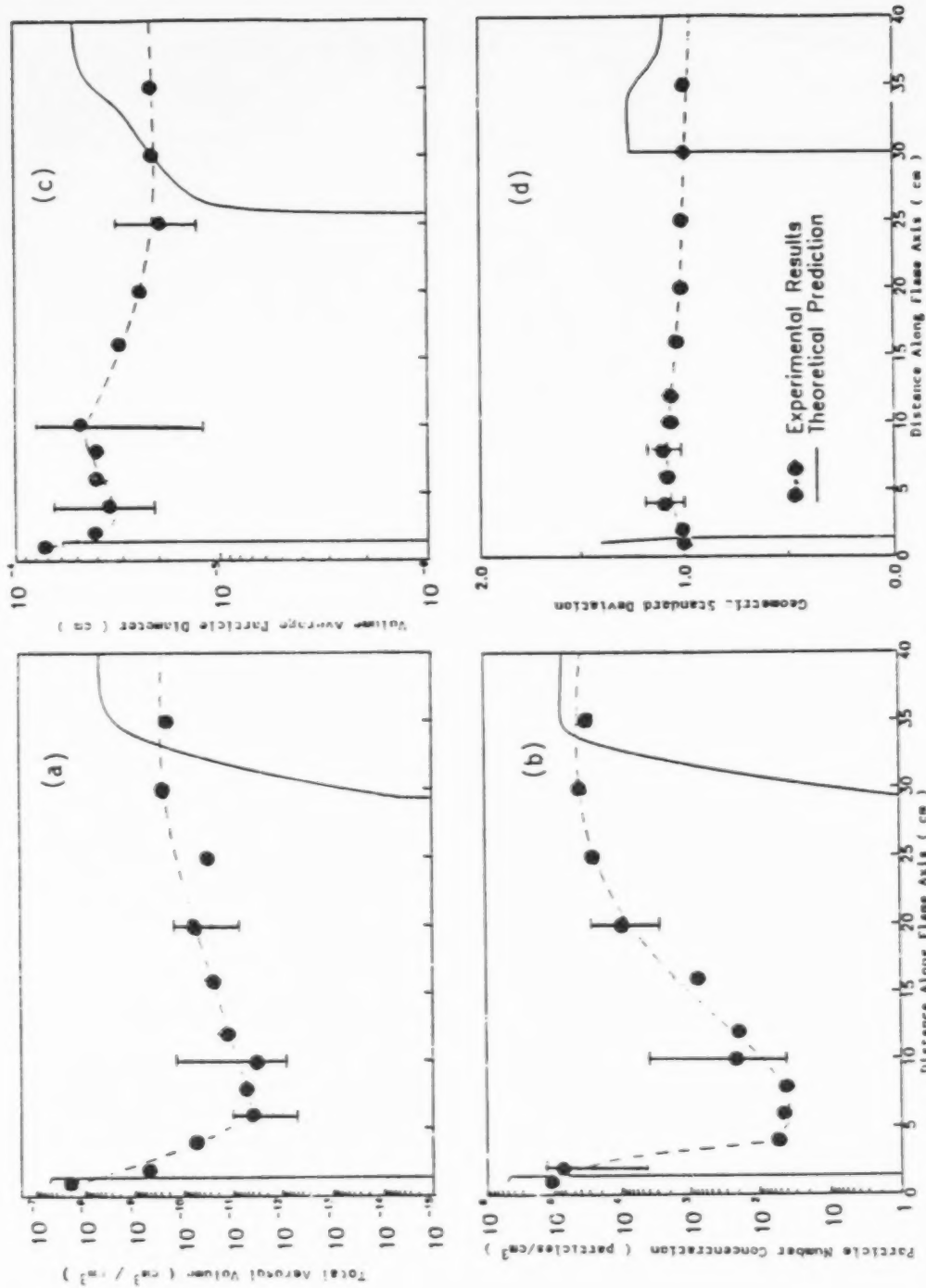


Figure 3. Lead aerosol characteristics as a function of distance along flame axis for an aerosol volume feed rate of $5.4 \times 10^{-3} \text{ cm}^3/\text{cm}^3$, geometric mean particle size of $0.5 \mu\text{m}$, and a geometric standard deviation of 1.4: (a) aerosol volume concentration, (b) number concentration, (c) volume average particle diameter, and (d) geometric standard deviation.

aerosol. Increases in number concentration and volume concentration in the post-flame region are observed to be close to the theoretically predicted values. The differences between predicted and measured values at locations closer to the inlet arise due to the limitations of the OPC in measuring particles smaller than $0.1 \mu\text{m}$. Better agreement between model predictions and experimental data is obtained later as the particles grow larger by vapor condensation and coagulation.

The results for the silicon tetrachloride experiments are plotted in Figures 4 (a) through (d). Silicon tetrachloride is oxidized to form silica, and the molecule itself is a thermodynamically stable particle (7). Hence, the reaction rate governs particle formation rates, and coagulation is the mode by which particles grow in the flame region. Significant differences are obtained between the theoretical and the predicted values of the aerosol volume and the number concentrations at initial locations. This again arises due to the limitation of the DMPS in measuring particles smaller than $0.05 \mu\text{m}$, and the silica particle when first formed is about $4 \text{ \AA}$ in diameter. Subsequently, the decrease in theoretically predicted number concentrations by coagulation agrees well with the experimental results as the particles grow to sizes that are readily detected by the DMPS.

In full scale incinerator systems, multiple elements are present. The vapors of the volatile metals (such as Pb) may condense onto the non-volatile particles (such as silica). Controlled experimental studies need to be performed with both compounds present simultaneously. The model has been used to predict Pb aerosol size distributions in the presence of seed particles, and nucleation of the volatile element was found to be completely quenched (6). This has important ramifications with regards to effective incinerator operation. By properly choosing design and operating conditions, one may effectively condense these volatile toxic species either homogeneously or on existing seed materials to grow large enough so that they can be efficiently captured in particulate control devices.

CONCLUSIONS

An experimental system to study particle formation and the evolution of the aerosol size distribution was developed. Experiments were performed with single components, and reasonable agreement was obtained with the predictions of a comprehensive model. Volatile elements nucleated to form tiny submicron particles in the downstream regions of the flame. Further growth of these particles occurred by rapid condensation of Pb vapor onto existing seed particles. When silicon tetrachloride was used as the test compound, stable silica particles were formed which grew by coagulation. In full scale incinerator systems, volatile and non-volatile elements are expected to be present, and hence condensation onto particles is expected to be a dominant mechanism. The theoretical model may be further developed for application in full scale

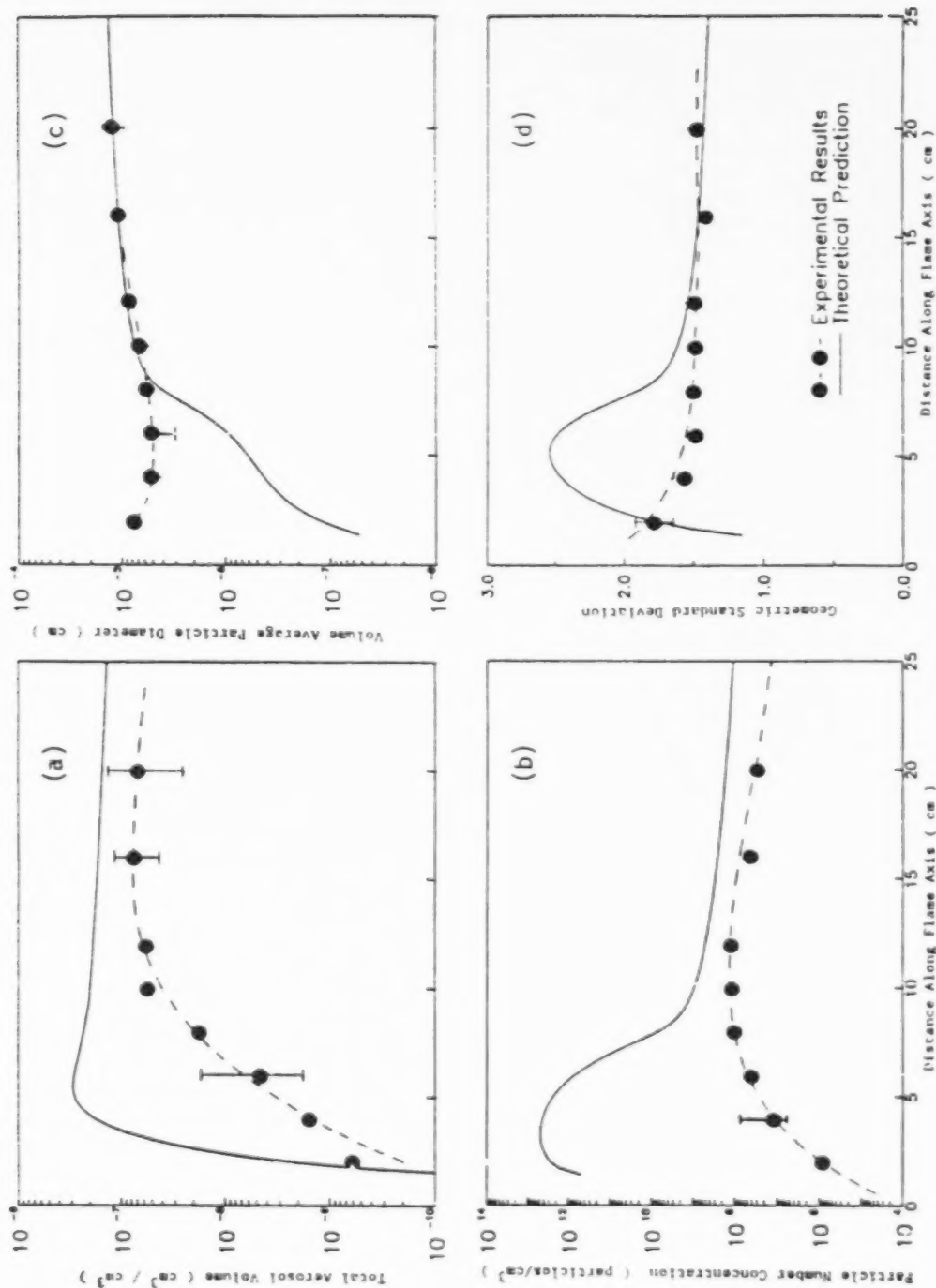


Figure 4. Silica aerosol characteristics as a function of distance along the flame axis for a vapor feed rate of 20 mg/min: (a) aerosol volume concentration, (b) number concentration, (c) volume average particle diameter, and (d) geometric standard deviation.

incinerators and used to determine operating conditions to achieve efficient capture of toxic elements.

ACKNOWLEDGEMENT

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FATE OF VOLATILES IN WASTEWATER TREATMENT

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ABSTRACT

Factors which affect the transport of volatile compounds from the aqueous phase to the gas phase by surface desorption (volatilization) and air stripping in conventional primary/activated sludge wastewater treatment plants are reviewed.

Fate of eleven volatile organic compounds spiked to pilot-scale activated sludge system was determined. Removals by sorption, volatilization and stripping, and biodegradation were assessed by measuring influent, effluent, primary and secondary sludges, and primary and aeration basin off-gas samples for the compounds studied.

INTRODUCTION

The fate of volatile organics in conventional primary/activated sludge treatment systems is controlled by several integrated removal mechanisms which operate simultaneously. The major mechanisms include: (a) sorption on solids and biomass, (b) volatilization to the atmosphere through surface desorption and air stripping, and (c) biodegradation or transformation by aerobic or anaerobic processes. Direct oxidation, hydrolysis, and other mechanisms may play a minor role in the removal of certain organic compounds. Sorption on wastewater solids has been correlated with the octanol/water partition coefficient and modified Randić indexes (1). The correlations developed are useful for modeling the role of sorption in a wastewater treatment plant. Volatilization and air stripping and the biological processes are more complicated and are controlled by compound specific properties, wastewater characteristics, and plant design and operational parameters. This paper will review some of the more important factors which control the fate of volatile compounds in wastewater plants with emphasis on air emissions from primary and activated sludge treatment systems.

FACTORS AFFECTING VOLATILE EMISSIONS

Several research studies which relate to the problem of air emissions from wastewater treatment plants have been reported (2-32). These studies have attempted to develop an understanding of the principles which affect the transport of volatile compounds from the aqueous phase to the gas phase by surface desorption (volatilization) and air stripping. Table 1 lists several factors which are important in air emissions from wastewater treatment plants. This section will discuss these factors in some detail.

TABLE 1. FACTORS AFFECTING AIR EMISSIONS

Aeration Rate
Henry's Law Constant
Acclimation
Biodegradation Rate Constant
Psi
Alpha
Aeration Device
Diffuser Type
Surfactants/Other Organics
Metabolism
Temperature

AERATION RATE

The effect of aeration rate on the stripping of volatiles from water and wastewater has been studied extensively. The effect is illustrated in Figure 1 where log concentration is plotted as a function of time for four different aeration rates from a 10-liter bioreactor without biomass (31).

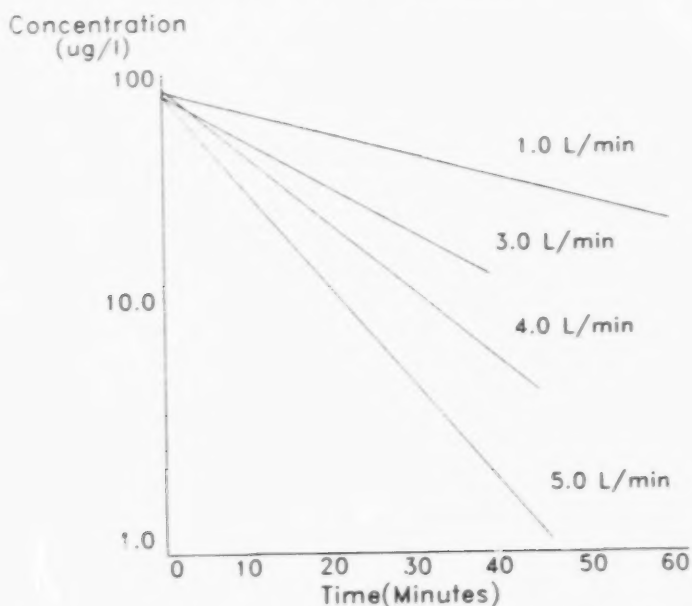


Figure 1. Effect of aeration rate on stripping of benzene without biomass.

Stripping rates were reproducible and not affected by initial concentrations. When comparing air emission data from different sources, the gas to liquid ratio will be an important factor.

HENRY'S LAW CONSTANT

Henry's Law Constant (H_c) is a critical parameter in overall stripping models for volatiles from wastewater treatment plants. Figure 2 (31) illustrates the observed correlation between H_c and stripping rates for selected volatile compounds.

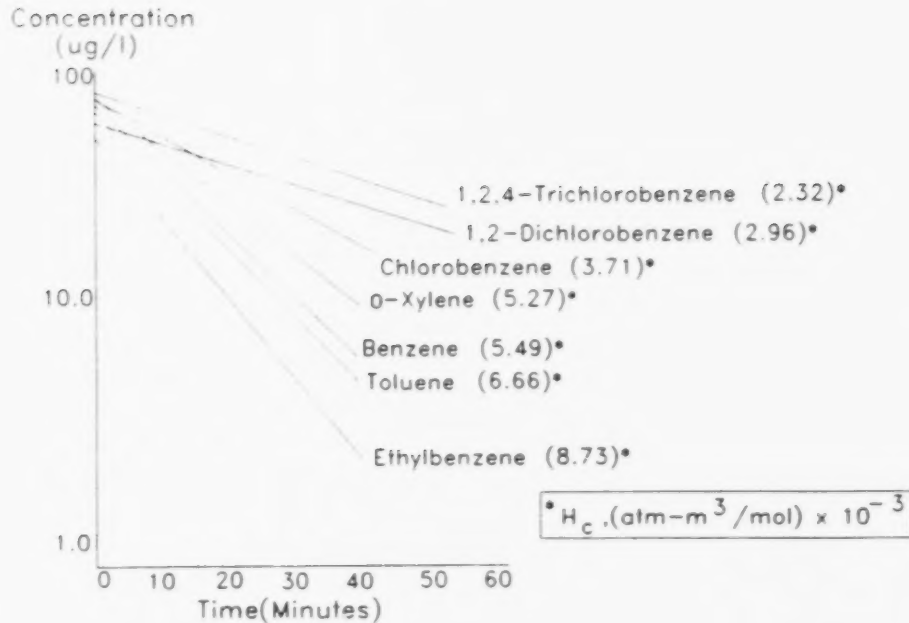


Figure 2. Effect of H_c on stripping of volatile organics.

In the absence of other factors, stripping of volatile compounds was directly related to Henry's Law Constant.

ACCLIMATION

When biota are exposed to compounds which are not readily degraded, adaptive changes can occur within the population which enable certain organisms to metabolize the substances. This process, known as acclimation, may take several days to several weeks or even longer to occur. Air emissions of volatiles are substantially reduced when the biomass is acclimated. The magnitude of this effect is shown in Table 2.

TABLE 2. EFFECT OF ACCLIMATION ON AIR EMISSIONS*

Compound	% Stripped	
	Unacclimated	Acclimated
Benzene	45	16
Toluene	40	17
Ethylbenzene	88	22
o-Xylene	90	25
Chlorobenzene	50	20

*Reference 31

Under acclimated conditions, biodegradation can compete effectively with volatilization and stripping as a removal mechanism and can significantly reduce the air emissions from wastewater treatment plants. An acclimated biomass can maintain the ability to degrade specific compounds if they are usually present in the influent wastewater. In the case of intermittent discharges, specific compounds may not be present in the influent wastewater for a period of time. Under these conditions, an acclimated biomass may lose the ability to degrade a given compound. However, if the component is again discharged within a reasonable period of time (i.e., less than 3 sludge retention times) the reacclimation process is substantially shortened as illustrated by the results summarized in Table 3.

TABLE 3. COMPARISON OF INITIAL ACCLIMATION AND REACCLIMATION AFTER 14 DAYS WITHOUT TOXICS ADDED TO INFLUENT*

Compound	Overall Removal (%)		Acclimation Period (Days)	
	Initial	Reacclimation	Initial	Reacclimation
Benzene	86	90	16-20	3-4
Toluene	81	88	16-20	3-4
Ethylbenzene	79	90	16-20	3-4
o-Xylene	78	81	16-20	3-4
Chlorobenzene	81	86	16-20	3-4

*Reference 31 (Sludge Retention Time 6 Days)

Approximately 2-3 weeks were required for initial acclimation compared

to 3-4 days for reacclimation for the compounds listed in Table 3.

BIODEGRADATION RATE CONSTANT

Volatilization and stripping of volatiles from a wastewater treatment plant are maximized if no competing mechanism contributes to the removal. However, for many compounds the biodegradation rate constant (K_b) is large enough so that this mechanism competes effectively with volatilization and stripping in the overall removal process. Under this condition, air emissions are substantially reduced. The effect of biodegradation rate constants on the fate of volatiles in two large wastewater treatment plants has been reported (28). Results for one of the plants are presented graphically in Figure 3.

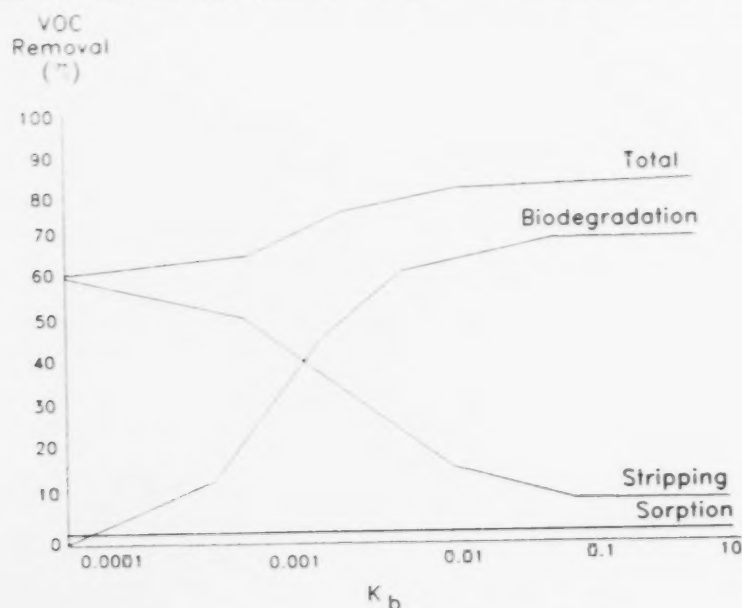


Figure 3. Effect of biodegradation rate constant on removal of volatiles.

As the biodegradation rate constant increases, the total removal of a given volatile compound increases, removal by stripping decreases, and sorption remains essentially constant.

PSI

Stripping can be defined as the transfer of organics at dispersed gas/water interfaces such as the surface of air bubbles produced by subsurface aerators. In this case, the rate of stripping can be defined as follows:

$$r_s = K_L^s a (C_{Li}^* - C_{Li}) \quad (1)$$

where $K_L^s a$ = overall mass transfer coefficient from the liquid phase
 C_{Li} = liquid phase concentration of compound i in equilibrium with the gas

phase C_{Li} = effluent concentration of compound i .

Since oxygen transfer for a given system can be measured, oxygen is used as a reference for expressing the mass transfer of other volatile organic compounds as shown in the following equation:

$$K_L^s a_i = \psi_i K_L a_{O_2} \quad (2)$$

where $K_L^s a_i$ = overall mass transfer coefficient of compound i
 ψ_i = transfer rate proportionality coefficient. The value of ψ_i can be measured or estimated from the relative diffusivity of the compound and oxygen using the following equation:

$$\psi_i = \left[\frac{D_i}{D_{O_2}} \right]^n \quad (3)$$

Measured values of n for selected volatile compounds ranged from 0.61 to 2.66 (17, 23). In Barton's model for stripping, n was assigned a value of 0.6 (29).

ALPHA

Alpha is an oxygen transfer correction factor. It is defined by the simple ratio of $K_L a$ in wastewater/ $K_L a$ in clean water. Standard procedures for oxygen transfer determinations have been described for both clean water (33) and wastewater (34).

AERATION DEVICES

Although most wastewater treatment plants use bubble or dispersed aeration systems, some do use surface aeration. Both systems have been modeled by several researchers cited in the reference section. In general, surface aeration achieves greater transfer of organic solutes to the atmosphere than does bubble aeration for a given oxygen transfer rate (24). The same authors reported that in bubble aeration the transfer efficiency of organic solutes decreases with increasing oxygen transfer efficiency when the overall transfer requirement is held constant.

DIFFUSER TYPE

Three levels of oxygen transfer efficiency, viz., 6%, 10%, and 15%, correspond to values for coarse, medium, and fine bubble diffused-air aeration, respectively, with a submergence depth of 4 meters (35). Since coarse bubble diffusers have the smallest percent oxygen transfer efficiency (6%), a higher gas/liquid ratio is required to maintain dissolved oxygen at the desired level. Under these conditions, stripping of volatiles is increased. As a consequence, the use of medium or fine bubble diffusers would decrease the emissions from a wastewater treatment plant.

SURFACTANTS/OTHER ORGANICS

The rate of mass transfer in aeration systems is strongly dependent on

wastewater composition. Low concentrations of surface active compounds in water have been shown to reduce the overall mass transfer coefficient, $K_L a$ (36-39). The effectiveness of porous diffusers has been shown to be increased significantly by organic constituents of wastewater such as phenols, alcohols, and acids. Alpha values approaching 3.0 have been observed in 0.1 millimolar acetic acid (40).

METABOLISM

Microorganisms can convert many toxic synthetic organic chemicals to inorganic products. These microbial processes can lead to environmental detoxification, the formation of new toxicants, or the biosynthesis of persistent products (41). Research has shown that the source of the highly volatile chloroethene compounds, vinyl chloride, vinylidene chloride, cis and trans 1,2-dichloroethene in a raw groundwater was the result of biodegradation of trichloroethylene and/or tetrachloroethylene which are found widely spread in the environment as a result of extensive use of these compounds (42). Both aerobic and anaerobic organisms were capable of degrading chlorinated solvents. In complex mixtures where several chlorinated or aromatic solvents are present, metabolism can result in the transformation of one compound into another. Under these conditions one can measure stripping efficiencies in excess of 100 percent. This effect will be discussed in more detail in a later section.

TEMPERATURE

The general expression for the volatilization rate constant K_v can be expressed in terms of the mass transfer rates of the compound across liquid and gas phase boundary layers. The general expression can be written as follows:

$$k_v = \frac{1}{L} \left[\frac{1}{k_l} + \frac{RT}{H_c k_g} \right]^{-1} \quad (4)$$

where L is the depth which equals the interfacial area, A , divided by the liquid volume, V ; k_l is the liquid film mass transfer coefficient; R is the gas constant; T is the temperature; H_c is the Henry's law constant; and k_g is the gas-film mass transfer coefficient (17). The two-film mass transfer model for volatilization has been reviewed and applied to environmental problems (43, 44). As shown by Equation 4, the rate constant for volatilization or stripping is directly proportional to temperature.

An understanding of the factors described in this section is essential for accurate estimates of volatile emission rates from wastewater treatment plants.

FATE OF VOLATILES IN CONVENTIONAL PRIMARY/ACTIVATED SLUDGE TREATMENT

The removal of volatiles by six wastewater treatment processes was studied by Hannah et al. (45, 46). The processes included conventional primary/activated sludge treatment. Weber and Jones (31) conducted bench-

full scale treatment plant data. None of the studies cited in this section measured loss of volatiles in primary treatment. The first attempt to develop fate-in-treatment data for a conventional primary/activated sludge system was reported by Bhattacharya et al. (47) for selected volatiles and semivolatiles.

In the present study, an attempt was made to obtain improved mass balance data for the fate of selected volatiles from the Resource Conservation and Recovery Act (RCRA) list of pollutants for both primary and secondary treatment processes. Two pilot-scale activated sludge systems were operated in parallel at the United States Environmental Protection Agency's Test and Evaluation Facility in Cincinnati, Ohio. One pilot plant was used as the spiked test system while the other served as an unspiked control. The eleven compounds selected for this study from the RCRA list of pollutants are shown in Table 4 along with physical-chemical properties.

TABLE 4. LIST OF SELECTED RCRA COMPOUNDS

Compound	CAS No.	TLV (ppm)	H _c (atm.m ³ /mole)	K _{ow}
Acetone	000-067-641	750	6.8 X 10 ⁻⁶	0.57
Cyclohexanone	000-108-941	25	2.5 X 10 ⁻⁵	6.46
Methyl ethyl ketone	000-078-933	200	5.8 X 10 ⁻⁵	N.A.
Tetrahydrofuran	0109199-9	200	1.1 X 10 ⁻⁴	5.4
Ethylbenzene	000-100-414	100	6.4 X 10 ⁻³	1412
Trichloroethylene	000-079-016	100	9.1 X 10 ⁻³	263
Carbon tetrachloride	000-056-235	10	2.3 X 10 ⁻²	436
1,1,1-Trichloroethane	000-071-556	450	3.0 X 10 ⁻²	310
Chlorobenzene	000-108-907	75	3.5 X 10 ⁻³	690
1,1,2-Trichloroethane	000-079-005	20	7.4 X 10 ⁻⁴	117
Tetrachloroethylene	000-079-016	50	1.5 X 10 ⁻²	759

H_c = Henry's Law Constant
N.A. = Not available

K_{ow} = octanol/water partition coefficient

MATERIALS AND METHODS

Two pilot-scale activated sludge systems were operated at a flow rate of 35 gpm (2.2 L/s) and a hydraulic retention time of 7.5 hours. An operational sludge retention time (SRT) of 4 days was used. The organics were added in a single spike mixture to produce concentrations of approximately 0.25 mg/L of each compound in the influent to the treatment system. The operating conditions and design characteristics for the two systems used in this study are shown in Table

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TABLE 5. OPERATING CONDITIONS AND DESIGN CHARACTERISTICS OF THE PILOT PLANT

I. Design Flow	= 35 gpm = 50,400 gpd
II. Primary Clarifiers	- Diameter = 9'-8" Weir Diameter = 9'-1" Surface Area = 73.4 ft ² Surface Overflow Rate = 687 gpd/ft ²
III. Aeration Basins	- L:W:D = 17'-7":10'-0":12'-0" Surface Area = 175.8 ft ² Volume = 15,780 gal. Residence Time = 7.5 hrs. Gas to Liquid Ratio = 34.2 Sanitaire Course Air Diffusers, Model D24
IV. Secondary Clarifiers	- Diameter = 11'-11" Surface Area = 111.5 ft ² Surface Overflow Rate = 452 gpd/ft ²

In order to sample the air space above the primary clarifiers, loosely fitted covers with a 1-inch (2.5-cm) gap at the edge were fabricated for the units. The covers were vented through a duct to the roof. An air sweep equivalent to a 4 kilometer per hour wind was maintained over the surface of each primary clarifier by exhausting air at 8,500 liters/minute. The aeration basins were fitted with airtight covers and the off gas was vented to the roof. The average air flow in each aeration basin was 4,250 liters/minute. Air samples were collected in stainless steel canisters and were analyzed by GC/MS by a contract laboratory (PEI Associates, Inc., Cincinnati, Ohio) using Method TO-14 (48). Sludge and liquid samples for RCRA analytes were measured using Method 1624 (49).

Automated analytical procedures were used for the conventional pollutants. These analyses (soluble chemical oxygen demand and ammonia nitrogen) were performed three times per week. Total and volatile suspended solids in the influents, effluents, and mixed liquors were measured daily using composite samples collected three times per day. All these parameters were measured following Standard Methods (50).

The test system was spiked for ten weeks. Following an acclimation period of three weeks, composite aqueous and sludge samples were collected

during a 24-hr. period once every week for seven weeks. Composite air samples were also collected during this 24-hr. test period. The average air flow rates were also determined for each sampling event. The wastewater flows, dissolved oxygen concentrations, and pH were checked by the operators three times per day.

RESULTS AND DISCUSSION

The average percent removals and standard deviations for the conventional pollutants during the test period are summarized in Table 6.

TABLE 6. AVERAGE PERCENT REMOVALS OF CONVENTIONAL PARAMETERS

PARAMETER	CONTROL SYSTEM PERCENT REMOVAL		SPIKED SYSTEM PERCENT REMOVAL	
	AVERAGE	STD DEVIATION	AVERAGE	STD DEVIATION
Total Suspended Solids	96	2	94	4
Volatile Suspended Solids	96	2	96	3
Soluble Chemical Oxygen Demand	69	11	69	14
Ammonia-Nitrogen	92	14	93	12

The spiked toxic organic compounds in the wastewater produced no significant effects on the treatment of conventional pollutants. Ammonia removals higher than 90% were achieved at an SRT as low as 4 days. Since this study was performed in the summer, high temperature probably enhanced nitrification. Nitrifiers are expected to be more adversely affected by toxicants than activated sludge organisms. High nitrification showed that the added organic compounds were not toxic to even the nitrifiers.

The fates of the volatile organic compounds were studied by measuring the concentrations of each spiked compound in the primary influent, primary effluent, secondary effluent, primary and secondary sludges, and primary and secondary air samples. Total removals for both primary and secondary treatment processes are summarized in Table 7 for the volatiles studied.

TABLE 7. SUMMARY TOTAL REMOVALS (PRIMARY + SECONDARY)

NAME OF COMPOUND	PERCENT TOTAL REMOVAL							AVERAGE	STANDARD DEVIATION
	EVENT 1	EVENT 2	EVENT 3	EVENT 4	EVENT 5	EVENT 6	EVENT 7		
Acetone	95.7	94.0	96.7	96.8	95.3	99.3	80.8	94.1	5.64
Methyl ethyl ketone	94.8	95.0	97.2	96.7	98.0	98.8	-	96.7	1.45
Cyclohexanone	95.0	-	-	92.4	77.0	-	66.8	82.8	11.52
Tetrahydrofuran	54.8	-	91.3	92.0	96.5	100.0	100.0	76.4	34.41
Carbon tetrachloride	98.2	98.8	99.2	98.4	99.6	99.3	98.1	98.8	0.52
1,1,1-Trichloroethane	97.4	98.1	98.7	98.6	99.2	98.9	99.2	98.6	0.60
1,1,2-Trichloroethane	59.3	66.2	69.3	68.9	78.3	79.4	74.1	70.8	6.55
Trichloroethylene	99.3	-	99.8	99.9	99.8	100.0	99.3	99.7	0.27
Tetrachloroethylene	95.7	96.0	97.8	97.7	98.8	98.3	97.0	97.3	1.07
Chlorobenzene	99.0	98.3	99.4	99.9	99.7	100.0	97.3	99.1	0.91
Ethylbenzene	99.1	94.6	97.7	99.2	100.0	99.8	97.5	98.3	1.75

(-) UNAVAILABLE DATA (Decomposed in sampling canister)

Total removals generally exceeded 90 percent (1,1,2-trichloroethane and tetrahydrofuran were the exceptions).

Removals by volatilization and stripping are presented in Table 8 for the combined primary and secondary processes.

TABLE 8. SUMMARY OF REMOVALS BY VOLATILIZATION AND STRIPPING (PRIMARY + SECONDARY)

NAME OF COMPOUND	PERCENT STRIPPED							AVERAGE	STANDARD DEVIATION
	EVENT 1	EVENT 2	EVENT 3	EVENT 4	EVENT 5	EVENT 6	EVENT 7		
Acetone	1.1	1.1	2.6	2.4	1.8*	1.8*	1.8*	1.8	0.81*
Methyl ethyl ketone	1.6	1.5	1.5	2.7	1.8*	1.8*	1.8*	1.8	0.59*
Cyclohexanone	-	-	-	-	-	-	-	-	-
Tetrahydrofuran	15.6	11.0	8.1	5.9	10.2*	10.2*	10.2*	10.2	4.19*
Carbon tetrachloride	117	129	61.7	125	107	95.6	83.3	103	22.5
1,1,1-Trichloroethane	122	137	94.3	111	106	105	85.5	109	15.9
1,1,2-Trichloroethane	16.2	29.0	23.9	38.0	51.5	52.0	48.6	37.0	13.3
Trichloroethylene	62.4	-	51.2	57.0	53.7	51.5	38.5	52.4	7.29
Tetrachloroethylene	122	158	81.0	108	108	120	78.7	111	25.0
Chlorobenzene	14.7	14.7	11.1	9.9	10.4	15.9	11.4	12.6	2.24
Ethylbenzene	16.9	23.0	16.5	13.3	12.0	16.0	13.9	15.9	3.32

(-) UNAVAILABLE DATA (Decomposed in sampling canister)

* AVERAGE VALUES AND STANDARD DEVIATIONS CALCULATED FROM FIRST FOUR EVENTS

Since both primary and aeration basin air samples were analyzed, the

data presented in Table 9 can be factored to describe air emissions for the separate processes. Percent volatilized in primary treatment and stripped in the aeration basin is shown in Table 9.

TABLE 9. AIR EMISSIONS FROM PRIMARY AND SECONDARY TREATMENT

NAME OF COMPOUND	PERCENT VOLATILIZED PRIMARY TREATMENT	STANDARD DEVIATION	PERCENT STRIPPED AERATION BASIN	STANDARD DEVIATION
Acetone	1.5	0.6	0.3	0.06
Methyl ethyl ketone	0.46	0.6	N.D.	N.A.
Cyclohexanone	-	-	-	N.A.
Tetrahydrofuran	3.3	0.1	6.9	3.6
Carbon tetrachloride	12.4	1.7	90.6	20.6
1,1,1-Trichloroethane	12.4	1.2	96.6	14.8
1,1,2-Trichloroethane	5.0	1.3	32.0	11.8
Trichloroethylene	10.2	0.7	42.2	8.2
Tetrachloroethylene	11.6	0.8	99.4	23.2
Chlorobenzene	8.8	0.7	3.8	2.1
Ethylbenzene	8.2	0.7	7.6	3.6

(-) UNAVAILABLE DATA (Decomposed in sampling canister)
N.D. = NOT DETECTED N.A. = NOT AVAILABLE

Air emissions from primary treatment were significant. The dominant factors which controlled the process were volatile compound properties (Henry's law constant and octanol/water partition coefficient) and the nature of the air water interface which is a function of process design parameters and wind speed. In the aeration basin, air emissions were largely controlled by the gas to liquid flow ratio and the magnitude of the biodegradation rate constant under the acclimated conditions used in this study.

The removal of volatiles by sorption and biodegradation were also assessed. A summary of the removals obtained by sorption is shown in Table 10.

TABLE 10. SUMMARY OF REMOVALS BY SORPTION (PRIMARY+SECONDARY)

NAME OF COMPOUND	PERCENT SORBED							AVERAGE	STANDARD DEVIATION
	EVENT 1	EVENT 2	EVENT 3	EVENT 4	EVENT 5	EVENT 6	EVENT 7		
Acetone	0.4	0.9	0.9	1.0	0.6	0.1	0.2	0.6	0.32
Methyl ethyl ketone	1.0	0.6	0.6	0.8	0.5	0.3	-	0.6	0.23
Cyclohexanone	2.2	-	-	-	0.2	-	0.6	1.0	0.88
Tetrahydrofuran	2.0	1.9	1.1	1.1	1.2	0.5	0.9	1.2	0.49
Carbon tetrachloride	1.1	0.9	0.6	0.8	0.1	0.4	0.1	0.6	0.38
1,1,1-Trichloroethane	1.0	2.3	1.8	1.4	1.2	1.8	2.5	1.7	0.52
1,1,2-Trichloroethane	1.8	2.5	2.0	1.8	1.7	2.3	2.3	2.1	0.30
Trichloroethylene	0.9	-	2.6	1.9	1.8	1.1	2.8	1.8	0.71
Tetrachloroethylene	1.2	4.4	2.4	2.4	1.0	2.3	3.8	2.5	1.17
Chlorobenzene	1.4	3.4	2.4	2.0	1.6	2.7	6.2	2.8	1.53
Ethylbenzene	2.3	5.2	5.1	2.9	2.4	4.7	13.1	5.1	3.46

(-) UNAVAILABLE DATA (Decomposed in sampling canister)

Sorption of volatiles by primary sludge and mixed-liquor solids accounted for 0.5 - 5 percent of the total removal in primary/activated sludge treatment. The sorption capacity of wastewater solids and sludges for organic compounds has been correlated with octanol-water partition coefficient. Capacities must be based on organic matter in the wastewater solids or sludges as measured by volatile solids (loss on ignition at 550°C) for predictive purposes (1).

The percent biodegraded can be estimated from mass balance considerations (% biodegraded = % total removal - % sorbed - % volatilized and stripped). Estimated removals by the biodegradation mechanism are presented in Table 11.

TABLE 11. SUMMARY OF ESTIMATED BIODEGRADATION

NAME OF COMPOUND	PERCENT BIODEGRADED (ESTIMATED)							AVERAGE	STANDARD DEVIATION
	EVENT 1	EVENT 2	EVENT 3	EVENT 4	EVENT 5	EVENT 6	EVENT 7		
Acetone	94.1	92.0	93.3	93.4	92.8	97.6	76.8	91.4	6.2
Methyl ethyl ketone	92.2	92.9	95.1	93.2	96.7	97.5	-	94.6	2.0
Cyclohexanone	92.8	-	-	92.4	76.8	-	66.3	82.1	11.2
Tetrahydrofuran	37.1	78.4	82.1	85.0	86.6	86.8	93.0	78.4	18.8
Carbon tetrachloride	-19.6	-31.4	37.0	-27.7	-7.9	3.4	14.8	-4.5	22.9
1,1,1-Trichloroethane	-25.2	-41.7	2.6	-13.7	-8.3	-7.9	11.2	-11.9	16.2
1,1,2-Trichloroethane	41.3	34.7	43.3	29.1	25.2	25.1	23.3	31.7	7.6
Trichloroethylene	36.0	-	46.1	41.0	44.3	47.4	58.0	45.5	6.7
Tetrachloroethylene	-28.0	-66.3	14.4	-12.6	-10.0	-24.1	14.4	-16.0	25.7
Chlorobenzene	82.8	80.2	85.9	87.9	87.7	81.4	79.6	83.6	3.2
Ethylbenzene	79.9	66.4	76.1	83.0	85.4	79.1	70.5	77.2	6.3

(*) % BIODEGRADED = % TOTAL REMOVAL - % SORBED - % STRIPPED

(-) UNAVAILABLE DATA (Decomposed in sampling canister)

Polar solvents (acetone, methyl ethyl ketone, cyclohexanone, and tetrahydrofuran) were removed primarily by biodegradation. Chlorinated aliphatic solvents showed little or no biodegradation (except for trichloroethylene). Volatilization and stripping to the atmosphere was the dominant removal mechanism. Aromatic solvents were removed primarily by biodegradation, however, volatilization and stripping accounted for approximately 15 percent of the total removal. Negative values for % biodegradation can be the result of analytical error in sample analyses or can be due to metabolism which produces the compound as a product of degradation of another component in the spike mixture or in the wastewater feed.

SUMMARY AND CONCLUSIONS

The eleven compounds spiked into the activated sludge system did not cause any adverse effect on plant performance including nitrification. Sorption accounted for 0.5 - 5% of the removal of volatiles. Total removal was greater than 94% for eight of the eleven compounds studied. The minimum removal was 70% for 1,1,2-trichloroethane.

Volatilization and stripping was the primary removal mechanism for carbon tetrachloride, 1,1,1-trichloroethane, and tetrachloroethylene. Polar solvents were biodegraded while the two aromatic solvents showed intermediate biodegradation with substantial (15%) emissions to the atmosphere.

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FIELD ASSESSMENT OF AIR EMISSIONS FROM
HAZARDOUS WASTE DEWATERING OPERATIONS

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ABSTRACT

Petroleum companies generate millions of tons of sludge every year from American Petroleum Institute (API) separators, Dissolved Air Floatation (DAF) float, and biological waste. This sludge is often dewatered to reduce the volume of solid waste that will require disposal. Since the sludge is derived from petroleum products, a variety of volatile and semi-volatile organics can be contained in the sludge mixture. Sludges are often heated and dewatering equipment is open to the atmosphere, therefore increasing the potential for the release of organics to the air from the dewatering process. Organic concentrations as high as 5,000 ppm have been found at the vents from the dewatering process. This paper presents the results of a comprehensive study that was performed for the EPA to quantify the release of volatile and semi-volatile organics from sludge dewatering operations. The study included field tests of three dewatering operations in which material balance was used to calculate air releases.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Sludge dewatering is a process used by industry to reduce the volume of waste before disposal. The sludge dewatering process involves extracting the liquid out of the sludge. After an exhaustive study of dewatering operations, it was found that only sludge dewatering operations at petroleum refineries contained concentrations of organic material over 500 ppm (1). These petroleum refinery waste sludges contain high concentrations of oil and organic chemicals and include API separator sludge, DAF float, and biological sludge. Both DAF and API sludge are considered hazardous waste (K048 and K051, respectively). Dewatering of refinery sludge may be a significant source of volatile organic emissions since few refineries utilize volatile organic emissions collection and/or control devices.

The U.S. Environmental Protection Agency (EPA) is currently collecting information to develop standards as necessary for the control of air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs). These field tests were conducted to aid in the development of standards for hazardous waste dewatering operations. The main objectives of this study were to:

- ° Determine the percent of volatile and semi-volatile organic compounds removed from the sludge during dewatering, and
- ° Determine the air emissions of volatile and semi-volatile organic compounds from the dewatering process.

This paper provides general information on the dewatering process and the types of dewatering methods currently in use, discusses the dewatering operations at the three refineries tested, and discusses the procedures and methods used to determine air emissions from the dewatering process.

DEWATERING METHODS

As mentioned earlier, the objective of sludge dewatering is to reduce the amount of liquid in the sludge, therefore, reducing the volume of waste that must be disposed. The input or sludge to the dewatering device is called the feed. The liquid removed from the feed (or sludge) is called the filtrate. The final product of dewatering is called the cake. There are four generally accepted ways to dewater sludge:

- ° centrifuge;
- ° vacuum filtration;
- ° plate and frame filtration; and
- ° belt press filtration.

A centrifuge accelerates sedimentation through the use of centrifugal force. In a centrifuge, a rotating bowl acts as a highly effective settling tank. The most common type of centrifuge used in sludge dewatering is the imperforate basket centrifuge which handles sludges with high solids content. Centrifuges are not used as readily as other dewatering devices due to high maintenance costs and problems with separating suspended solids.

Vacuum filters use atmospheric pressure as the driving force which causes the liquid phase to move through a porous media and separate from the solids. Vacuum filtration consists of a large cylindrical drum which rotates through a vat containing sludge. The drum rotates through three zones. In the cake forming zone, a vacuum is applied to the submerged section of the drum which causes the filtrate to pass through the porous surface media and cake to form on the surface of the drum. As the drum rotates, it is carried to the cake drying zone. This zone is also under vacuum and further dries the cake. As the drum rotates further, it is carried into the cake discharge zone where the vacuum is removed and the cake is scraped off the drum. The last few years have seen a decline in the use of the vacuum filter due to improvements in other dewatering methods which make them more economical and technically feasible.

Plate and frame filters use fluid pressure generated by pumping sludge into the unit as the driving force to separate solids from liquids. Plate and frame filters (or recessed plate pressure filters) are constructed from a series of recessed plates. As more sludge is pumped into the filter, the pressure increases causing the filtrate to pass through the filter cloth leaving the cake. Plate and frame filters are used for sludges of poor dewaterability or for cases where a high solids content cake is required. Plate and frame filters are operated on a batch process and do not run continuously.

Belt filter presses employ single and double moving belts to dewater sludges continuously. Any belt filtration process includes three basic operational stages: chemical conditioning of the feed, gravity drainage to a non-fluid consistency, and compaction of the pre-dewatered sludge. A majority of refineries dewatering waste use the belt filter press because of its ability to handle high sludge throughput capacities.

DEWATERING PROCESSES FOR THREE SELECTED FACILITIES

Five facilities across the country were visited to observe and review their sludge dewatering processes. The following three sites were selected for testing because the sludge feed contained a significant concentration of organics:

- ° Sun Refining and Marketing Company - Toledo, Ohio
- ° British Petroleum Refinery - Lima, Ohio
- ° Sun Refining and Marketing Company - Tulsa, Oklahoma

SUN REFINING AND MARKETING COMPANY - TOLEDO, OHIO

Sun Refining and Marketing Company in Toledo, Ohio (Sun-Toledo) has two processing units with a total throughput of 120,000 barrels per day (1). As a result of their production facilities, they produce API bottoms from the API separator, DAF float from the air flotation unit, and biological sludge. The filter cake is landfilled and the filtrate is sent to the wastewater treatment plant.

Sun-Toledo has one belt filter press which processes approximately 20,000 gallon per day (gpd) of sludge and generates approximately 18 tons per operating day of cake. The press operates 4 days per week. API and DAF sludges are mixed and dewatered in the press. Biological sludges are also dewatered in this press, but are kept separate from the API and DAF wastes.

The sludges go through a series of mixing and treatment processes before being dewatered. The API and DAF sludges are mixed in two large 1-million gallon tanks where the sludge is steam heated to 100°F. Large capacity pumps agitate the sludge and transfer it to the oily waste feed tank. Once in the oily waste feed tank, the sludge is heated to 140°F and pumped to the belt filter press. A conditioning polymer is added to the sludge before it is pressed. The belt filter press is fed at approximately 35 gallons per minute. During filtration, the belt is backwashed with water. The filter cake from the belt press filter is then conveyed to the cake storage bins, after which it is landfilled. The filtrate is collected and sent to the waste water treatment plant. A side draft hood, located on the wall, ducts air to a carbon filter and exhaust fan on the roof. Figure 1 illustrates the dewatering process.

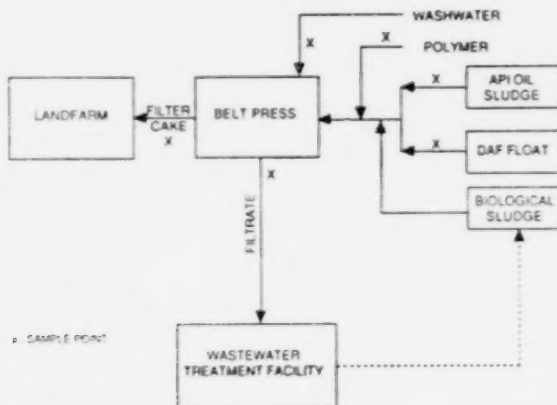


Figure 1. Dewatering Process at Sun Refining - Toledo, Ohio.

BRITISH PETROLEUM REFINERY - LIMA, OHIO

British Petroleum Refinery in Lima, Ohio (BP-Lima) produces gasoline, diesel fuel, jet fuel, kerosene, lube oil, and benzene (2). As a result of their production facilities, they produce API bottoms from the API separator, DAF float from the air flotation unit, and biological sludge which must be dewatered to reduce its volume before disposal. The filter cake is disposed of on a land farm, and filtrate is sent to the waste water treatment plant.

BP-Lima uses a belt filter press for its dewatering operations. The press operates 24 hours per day, 7 days per week. About 40 continuous hours of this is spent dewatering biological sludge from the clarifier bottoms. During the balance of the time, oily sludge from the API separators and DAF float is dewatered. This sludge contains about 1-3 percent solids and has a pH of 6.5. The sludge is preheated to approximately 130°F and a conditioner polymer is added before being dewatered. As the sludge is dewatered, the filtrate drains from the press into a drainage hole below the filter. The filter cake is conveyed to a cake bin. Trucks transport the cake to the landfarm. Wash water is sprayed on the filter belts as they return to the front of the press. Air emissions from the process are vented through a stack in the roof. Figure 2 illustrates the general process flow for the dewatering unit.

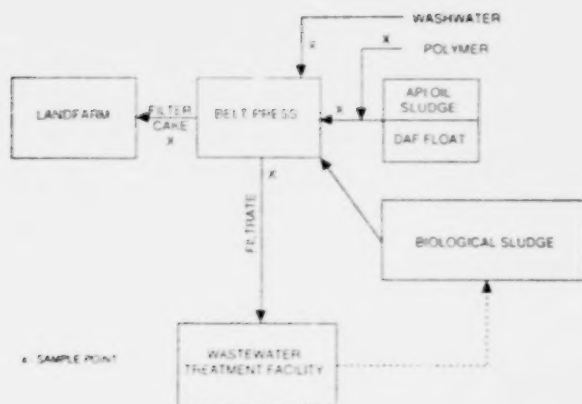


Figure 2. Dewatering Process at BP Refinery - Lima, Ohio.

SUN REFINING AND MARKETING COMPANY - TULSA, OKLAHOMA

Sun Refining and Marketing Company (Sun-Tulsa) in addition to producing typical fuel products produces benzene, toluene, propylene, and cyclohexane (3). As a result of their production facilities, they produce API bottoms from the API separator, DAF float from the air flotation unit, and biological sludge which must be dewatered to reduce its volume before disposal. The filter cake is disposed of to an onsite land farm and the filtrate is sent to an oil-water separator to recover the oil.

Sun-Tulsa has two belt presses housed in the refinery's belt press building. Each belt press is 2.2 meters wide and operates on an as needed basis which is approximately one shift per day. These presses were installed in 1986 to replace centrifuges. The centrifuges were replaced because solids in the sludges were reduced to fine particles, leading to Total Suspended Solids problems. In addition, down time was excessive.

The sludge dewatering process is shown in Figure 3. The sludge charge is stored in one of two 2,015-barrel charge tanks where it is heated before being pumped to the belt press. A polymer solution, Amerfloc Plus 5485, is injected from a 4,000 gallon tank into the feed line. At the belt press, the sludge is sprayed with wash water to aid in filtration. The filtrate exits the bottom of the belt press through a drain and flows to an oil-water separator. The filter cake is then conveyed to a cake bin and transported to the landfarm by trucks. Air emissions from each press are vented to a carbon filter and exhaust fan on the roof.

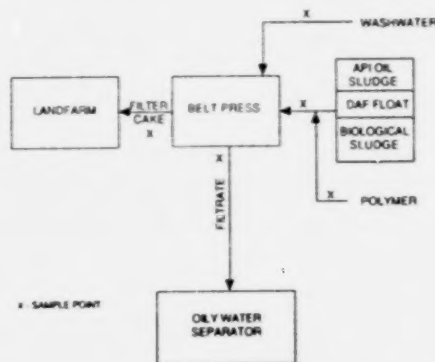


Figure 3. Dewatering Process at Sun-Tulsa, Oklahoma.

TESTING METHODS AND RESULTS

As discussed previously, the objectives of the field tests were to determine the percent of volatile and semi-volatile organics removed from the sludges during dewatering and to estimate the air emissions during the dewatering process. To meet these objectives, samples of the feed, filtrate, wash water, polymer, and cake were collected and analyzed for volatile and semi-volatile organic compound concentrations. Flow rates for all inlet and outlet streams were measured by reading flow meters or collecting a known quantity of material for a fixed time period. Biological sludge was not sampled because of its typically low concentration of organic compounds. Figures 1 through 3 show the sample locations at each refinery.

At the BP-Lima and Sun-Tulsa facilities, three 3-hour runs were conducted. At the Sun-Toledo facility, two 6-hour runs were conducted: one with API feed and one with DAF feed. Samples were collected and flow rates were measured at half-hour intervals during each run. Table 1 shows the measured feed rates for each of the field tests.

TABLE 1. MASS FLOW RATES FOR INFLUENT AND EFFLUENT STREAMS (lb/h)

	Feed	Polymer	Wash water	Cake	Filtrate
SUN-TOLEDO					
API test	20,820	823	16,127	2,617	--
DAF test	8,110	971	15,938	1,135	--
BP-LIMA					
Run 1	41,718	442	13,032	1,188	68,914
Run 2	40,410	1,529	12,726	576	34,358
Run 3	43,104	332	12,960	852	44,138
Average	41,744	768	12,906	872	49,137
Std. Dev.	1,100	540	131	250	14,543
SUN-TULSA					
Run 1	18,402	4,252	49,758	1,860	27,571
Run 2	25,716	3,345	49,818	300	39,127
Run 3	20,466	3,204	50,676	1,800	32,327
Average	21,528	3,600	50,084	1,320	33,008
Std. Dev.	3,079	464	419	722	4,742

Samples of the feed and wash water streams were collected from valve openings. The polymer was sampled by scooping the polymer solution from its feed tank. The filter cake was collected from the conveyor at the outlet of the filter press. The filtrate was collected by holding a large sample jar under the belt press where the filtrate drains. Homogeneous filtrate samples were difficult to sample and analyze because the oily mixture would immediately begin to separate. At the Sun-Toledo facility, the filtrate could not be measured

because the flow was too widespread across the belt to collect and measure. The filtrate at the BP-Lima facility was also difficult to measure. As a result lithium chloride was pumped into the filtrate and sampled at the inlet and outlet points. The ratio of the concentrations determined the filtrate flow rate.

Stack tests were conducted on the exhaust from the dewatering process. Volatile organics were collected from the exhaust stream with charcoal sorbents. Semi-volatile organics were collected using the modified Method 5 train with an XAD-2 sorbent. Total hydrocarbons were measured with a flame ionization analyzer. All analytical methods were taken from the third edition of SW-846. Method 8240 was followed for all volatile organic analyses, and Method 8270 was used for all semi-volatile organic analyses. Both methods employ gas chromatography and mass spectroscopy (GC/MS) techniques.

Tables 2 and 3 show the average mass flow rates of the volatile and semi-volatile organics, respectively, in the influent stream (feed, wash water, and polymer) and out the stack for each facility. At the Sun-Toledo facility, only one run was conducted on each sludge type, DAF and API, therefore standard deviation calculations are not applicable.

TABLE 2. MASS FLOW RATES OF VOLATILE ORGANICS (lb/h)

	Sun-Toledo				BP-Lima				Sun-Tulsa			
	Feed		Stack		Feed		Stack		Feed		Stack	
	API	DAF	API	DAF	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Xylenes	17	7.5	ND	ND	17	8.8	0.80	0.14	9.6	2.7	1.6	0.43
1,2,3-Trimethyl benzene	NT	NT	NT	NT	4.01	1.8	0.06	0.01	3.5	0.28	0.20	0.00
1,3,5-Trimethyl hexane	NT	NT	NT	NT	NT	NT	NT	NT	2.7	2.0	ND	--
Ethylbenzene	2.3	0.99	0.40	0.14	3.3	1.9	0.20	0.04	NT	NT	NT	NT
Methyl cyclohexane	10	4.8	2.8	1.1	4.5	2.2	0.94	0.33	1.8	1.8	2.0	1.3
n-Heptane	12	5.2	3.8	1.4	4.1	2.0	1.3	0.47	3.8	3.0	3.3	2.8
n-Hexane	NT	NT	NT	NT	NT	NT	NT	NT	3.5	3.8	4.3	5.1
Toluene	15	4.8	3.7	0.81	12	6.5	1.4	0.43	9.2	6.8	3.3	2.5
Benzene	2.1	0.68	0.80	ND	1.4	0.80	0.29	0.09	1.6	1.6	0.35	0.35
Ethyltoluene	2.8	1.7	0.17	0.10	10	4.9	0.24	0.04	7.5	0.43	0.45	0.07

ND = Not detected.
NT = Not tested.

TABLE 3. MASS FLOW RATES FOR SEMI-VOLATILE ORGANICS (lb/h)

	Sun-Toledo				BP-Lima				Sun-Tulsa			
	Feed		Stack		Feed		Stack		Feed		Stack	
	API	DAF	API	DAF	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Naphthalene	0.23	0.20	0.010	0.10	4.6	2.0	0.011	0.0022	6.0	0.42	0.09	0.014
2-Methyl naphthalene	NT	NT	NT	NT	14	6.6	0.0085	0.0018	23	3.54	0.17	0.042
Fluorene	NT	NT	NT	NT	1.8	0.90	9.0E-5	1.0E-5	1.7	0.35	<0.01	--
Phenanthrene	NT	NT	NT	NT	6.1	2.7	7.0E-5	1.0E-5	3.7	0.57	<0.01	--
Pyrene	NT	NT	NT	NT	3.7	1.5	1.0E-5	1.0E-5	NT	NT	NT	NT
n-Nitrosodi-phenylamine	NT	NT	NT	NT	ND	--	ND	--	7.9	1.6	ND	--
Dibenzofuran	NT	NT	NT	NT	NT	NT	NT	NT	ND	--	<0.01	--
Chrysene	0.060	0.030	ND	ND	NT	NT	NT	NT	NT	NT	NT	NT
1,3,5-Tri-methylbenzene	0.75	0.57	0.090	0.090	NT	NT	NT	NT	NT	NT	NT	NT

NT = Not tested.
ND = Not detected.

Volatile and semi-volatile organic emission factors, calculated from the data in Tables 2 and 3, are shown in Tables 4 and 5. The emission factor for each chemical is the ratio of the flow rate out the stack to the flow rate in the feed. This represents the fraction of each organic that would be released to the air. For example, the emission factor for xylenes at the BP-Lima facility was calculated as 0.046 lb/lb feed. Therefore, 4.6 percent of the xylene that was fed to the belt press was released out the stack.

TABLE 4. AIR EMISSION FACTORS FOR VOLATILE ORGANICS (lb/lb feed)

	Sun-Toledo		BP-Lima	Sun-Tulsa
	API	DAF		
Xylenes	ND	ND	0.046	0.19
1,2,3-Tri-methylbenzene	NT	NT	0.015	0.071
1,3,5-Tri-methylhexane	NT	NT	NT	ND
Ethylbenzene	0.17	0.14	0.061	NT
Methylcyclohexane	0.28	0.23	0.21	0.78
n-Heptane	0.32	0.28	0.31	0.92
n-Hexane	NT	NT	NT	1.3
Toluene	0.25	0.17	0.12	0.39
Benzene	0.38	ND	0.21	0.26
Ethyltoluene	0.061	0.059	0.024	0.073

ND = Not detected.
NT = Not tested.

TABLE 5. AIR EMISSION FACTORS FOR SEMI-VOLATILE ORGANICS (lb/lb feed)

	Sun-Toledo		BP-Lima	Sun-Tulsa
	API	DAF		
Naphthalene	0.044	0.50	0.0024	0.018
2-Methyl-naphthalene	NT	NT	0.00057	0.0087
Fluorene	NT	NT	0.000050	0.00057
Phenanthrene	NT	NT	ND	0.00017
Pyrene	NT	NT	ND	ND
n-Nitrosodi-phenylamine	NT	NT	ND	ND
Dibenzofuran	NT	NT	NT	NT
Chrysene	ND	ND	NT	NT
1,3,5-Tri-methylbenzene	0.12	0.16	NT	NT

ND = Not detected.

NT = Not tested.

SUMMARY

Dewatering is used by industry to reduce the volume of hazardous waste sludges before disposal. Common dewatering equipment include the centrifuge, the vacuum filter, the plate and frame filter, and the belt press filter. Based on an industry survey, the belt press filter is the most common dewatering device.

During hazardous waste dewatering, organics may be released to the air. In order to quantify these emissions, PEI conducted field tests at three petroleum refineries that use belt presses to dewater API and DAF sludges. Samples of the influent and effluent streams were taken and analyzed for volatile and semi-volatile compounds. Stack tests were also conducted on the exhaust gas.

The results of the field tests were used to determine the organics mass flows in the influent and effluent streams. Some major points from the results are as follows:

The highest influent mass flow of volatile and semi-volatile organics in the feed streams tested were 17 lb/h for xylenes and 15 lb/h for 2-methylnaphthalene.

The highest air emission rates for the volatile organics tested were 3.8 lb/h for n-heptane and 3.7 lb/h for toluene.

The highest emission rate for the semi-volatiles tested was 0.13 lb/h for 2-methylnaphthalene.

The tested organics with the highest air emission factors (lb released to the air/lb feed) were n-hexane, n-heptane, and naphthalene.

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BENCH-SCALE WET AIR OXIDATION OF COMPLEXED METAL CYANIDE SLUDGES

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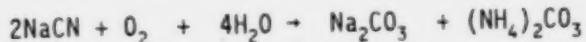
ABSTRACT

Certain aqueous and solid hazardous wastes from metal finishing and electroplating operations contain metal-cyanide complexes which must receive treatment to significantly reduce the cyanide concentrations prior to final disposal. The applicable processes for treating the cyanide wastes include alkaline chlorination, electrolytic oxidation, ultraviolet light/ozone, hydrolysis, and wet-air oxidation (WAO). Resource Conservation and Recovery Act (RCRA) wastes F006, F007, and F019 were treated by wet-air oxidation to determine the degree of cyanide destruction as measured by the total and amenable cyanide concentrations in the oxidized effluent and filtered solids.

INTRODUCTION

Wet-air oxidation (WAO) is the liquid phase oxidation of organics or oxidizable inorganic compounds at elevated temperatures and pressures. The oxidation is brought about by combining a wastewater or dilute sludge with a gaseous source of oxygen (air) at temperatures of about 175 to 327 degrees Centigrade (347° to 620° F) and pressures of about 2069 to 20,690 kPa (300 to 3000 psig).

Wet-air oxidation has been demonstrated at bench-scale, pilot-scale, and full-scale as a technology capable of breaking down hazardous compounds to carbon dioxide and other less toxic end products. The cyanides in electroplating wastes are converted to carbonate and ammonium ions when oxidized as shown by the following reaction:



High cyanide wastestreams (greater than 1%) have been successfully treated with WAO and destructions of more than 99% are typical. (1) This paper presents the results obtained from bench-scale oxidation testing to provide data for three RCRA wastes:

- F006 - wastewater treatment sludges from electroplating operations
- F007 - spent cyanide plating bath solutions
- F019 - wastewater treatment sludges from the chemical conversion coating of aluminum

CYANIDE TERMS

The characterization of cyanide species by ion structure include simple and complex cyanides. In solution, the simple cyanide compounds dissociate into the cyanide anion, and the complex cyanides dissociate into a cyanide-metal anion. Another category of cyanide is called "free cyanide", which is the sum of the cyanide anions and hydrogen cyanide in solution.

Amenable cyanide refers to the cyanide species removable by alkaline chlorination. This procedure is described in SW-846 Methods 9010 and 9012. (2) The total cyanide generally includes all cyanide groups, free, simple and cyanide-metal complexes, except cobalt, gold and some of the platinum group metals.

WASTE CHARACTERIZATIONS OF WAO TEST MATERIALS

The F006 filter cake was generated by treatment of spent solutions from barrel and rack plating lines dedicated to nickel-chromium, nickel-copper, cadmium, and chrome plating. The treatment system consists of chromium reduction, single-stage alkaline chlorination, neutralization, flocculation, sedimentation, sand filtration, sludge thickening, and filter press dewatering. The F006 contained a chemical oxygen demand (COD) of 37,000 mg/L, 400 mg/L total cyanide and total solids of 45 percent.

The F007 plating bath solution for wet-air oxidation tests was obtained from a manufacturer of decorative hardware, with brass, copper, zinc, nickel, and chrome plated products. The spent plating bath had a COD of approximately 33,000 mg/L, 24,000 mg/L total cyanide, and suspended solids of 15,850 mg/L (about 16 percent).

The F019 filter cake samples were obtained from a manufacturer of automotive refrigeration systems. The process wastewaters received treatment to reduce hexavalent chromium to trivalent, adjust the pH, precipitate metals and dewater the sludge. The samples contained 43,000 mg/L COD, about 5,000 mg/L total cyanide (as ferricyanide, $\text{Fe}(\text{CN})_6^{-3}$), and about 40 percent total solids.

WET AIR OXIDATION EXPERIMENTAL PROCEDURE

The tests were conducted at Zimpro/Passavant in their 0.5-liter capacity titanium shaking autoclave. Oxidations were performed for each waste at temperatures of 200°, 240°, and 280° C and a residence time of about 1 hour. The F006 was diluted 1:10 (volume) and potassium hexacyanoferrate added to restore the sample to approximately the original cyanide concentration. The F007 test was conducted on a 1:1 dilution, while the F019 was diluted 1:4.

Pressures were determined by the amount of air charged to the autoclave. After charging with a dilute waste sample and enough air to provide 120% of the F006 waste's oxygen demand (150-200 psig air charged), the autoclave was placed in a heater/shaker for the duration of the test. The autoclave was then cooled, the contents filtered, and both fractions analyzed.

TEST RESULTS

The results of the autoclave oxidations of F006, F007 and F019 are presented in the following tables. Compared to the dilute wastes, the COD reductions were in the range of 92-95% for the F006, 79-86% for the F007, and 68-83% for the F019. The total cyanide reductions in the filtrates were in the range of 78-99% for the F006, 99-99.5% for the F007, and 98-99.9% for the F019. The ammonia-nitrogen from the cyanide oxidations reached a maximum of about 300 mg/L for the F006 at the 240° and 280°C tests, 5000 mg/L for the F007 200°C test, and about 760 mg/L for the F019 280°C test.

The total cyanide values shown for "cake" samples represent only a small contribution to the values for the filtrates. When both filtrate and solids are considered together, the cyanide destruction values given in the tables for the filtrates are representative. For example, the total and amenable cyanide analysis of the F006 solids was 102 ug/g (ppm) at 200°C. The cyanide in the solids would contribute only 1.5 mg/L total cyanide to the 26.3 mg/L value for the filtrate and the total cyanide destruction remains nearly 78%.

DISCUSSION

Difficulties were encountered with the initial cyanide analyses for the three wastes. The measured total cyanide concentration of the F019 was about 2500 micrograms per gram as received from the waste generator. A value of 5000 micrograms per gram was reported by another laboratory. After a four to one dilution, the cyanide concentration of the waste was about 300 milligrams per liter---much lower than the calculated value, which was either 1250 or 625 milligrams per liter, depending on which initial value was used.

For the F006 test, about 40 milligrams per liter cyanide came from the diluted filter cake (ten to one) plus 315 milligram per liter cyanide from addition of potassium hexacyanoferrate. The analyses of the slurry indicated about 120 milligrams per liter cyanide, about 35 percent of the expected value.

It was recently noted that the SW-846 method 9010 for cyanide does not specify the sample size or distillation time. This could have been a factor in the variability of the results. Certain compounds can also interfere with the analysis (thiocyanate, sulfides, nitrates) and storage of the sample can result in inaccuracies in the determination of cyanide. However, we were not able to identify the specific reasons for these inconsistencies in the WAO tests.

CONCLUSION:

Even though there were apparent difficulties with the cyanide analytical method, the data from the wet-air oxidation treatment tests indicate significant destruction of the cyanides. It was also determined that the oxidized liquor would require subsequent treatment to remove the residual ammonia, any organic compounds and dissolved heavy metals.

TREATMENT STANDARDS FOR F006, F007, F019

Wet-air oxidation is the treatment technology proposed for F019. (3) However, final treatment standards for F006, F019 and F007 wastewaters are based on the performance of alkaline chlorination for the amenable and total cyanides, and chromium reduction followed by chemical precipitation using lime and sulfides and sludge dewatering for the metal. The total cyanide treatment standard concentrations required by RCRA are 590 milligrams per kilogram.

REFERENCES

1. Sittig, M. 1973. Pollutant Removal Handbook, Noyes Data Corporation. Pack Ridge, NJ
2. U.S. EPA, 1986. "Test methods for Evaluating Solid Wastes," (SW-846), Office of Solid Waste, Washington, DC
3. "Land Disposal Restrictions for Third Scheduled Wastes," November 22, 1989, Federal Register, pp. 48372-48529

TABLE 1. WET-AIR-OXIDATION RESULTS FOR F006

Parameter	Autoclave Feed	Oxidized product			
		Filtrate	Cake	Filtrate	Cake
Oxidation temp, °C	-	200	200	240	240
Time at temp, min	-	60	60	60	60
COD, g/L	3.7	0.166	197	0.269	24
COD reduction, %	-	95.5	-	93	-
pH	11	9.9	-	9.7	-
NH ₃ -N, mg/L	-	203.60	-	305.1	-
Total solids, g/L	17.3	1.92	100%	1.25	100%
Total ash, g/L	15.9	1.77	85.3%	1.17	86.6%
Cyanide, total, mg/L*	122.4	26.3	102 µg/g	0.82	20 µg/g
Total cyanide reduction, %	-	78	-	99	-
Cyanide amenable, mg/L	73.9	26.3	102 µg/g	0.82	20 µg/g
Amenable CN reduction, %	-	64	-	99	-
Sulfides, mg/L	<1	<1	-	<1	-
Fluoride, mg/L	3.59	2.12	0.69 mg/g	1.8	0.7 mg/g
Arsenic, µg/L	<1.2	<5.0	<2400 µg/g	<5.0	<2400 µg/g
Antimony, µg/L	<5.0	<5.0	72.8 µg/g	<5.0	84.8 µg/g
Barium, mg/L	0.54	0.17	40 µg/g	0.17	43 µg/g
Beryllium, mg/L	<0.01	0.018	0.28 µg/g	0.014	<0.2 µg/g
Cadmium, mg/L	220.5	0.53	241 mg/g	0.25	254 mg/g
Chromium (T), mg/L	348.4	44.4	29 mg/g	16.7	31 mg/g
Chromium (+6), mg/L	Interference	33.8	1980 µg/g	15.3	830 µg/g
Copper, mg/L	729.1	25.9	78 mg/g	5.4	85 mg/g
Iron, mg/L	1177	0.73	9.5 mg/g	0.07	10.1 mg/g
Lead, mg/L	1.12	<0.5	48 µg/g	<0.5	103 µg/g
Mercury, mg/L	0.42	2.05	1.1 µg/g	5.14	0.12 µg/g
Nickel, mg/L	643.9	2.4	62 mg/g	0.12	63 mg/g
Selenium, mg/L	<0.2	38	<4000 µg/g	19	<4000 µg/g
Silver, mg/L	<0.05	<0.05	<1 µg/g	<0.05	<1 µg/g
Thallium, mg/L	<5.0	40	<14 µg/g	50	<14 µg/g
Vanadium, mg/L	<0.05	<0.05	<1 µg/g	<0.05	<1 µg/g
Zinc, mg/L	355.1	0.44	33 mg/g	0.26	35 mg/g

* except as noted

TABLE 2. WET-AIR-OXIDATION RESULTS FOR F007

Parameter	Raw Waste	Dilute Waste*	Filtrate	Solids	Filtrate	Solids	Filtrate	Solids
Oxidation temp, °C			200	200	240	240	280	280
COD, mg/L	33,370	16,685	3,060	-	2,315	-	3,578	-
COD reduction, %	-	-	81.7	-	86.1	-	78.6	-
Cyanide (T), mg/L	23,667	11,834	117	183 µg/g	86	<1.0 µg/g	58	<1.0 µg/g
Cyanide (T), red., %	-	-	99.0	-	99.3	-	99.5	-
Cyanide (A), mg/L	21,750	10,875	114	143 µg/g	86	<1.0 µg/g	55	<1.0 µg/g
Cyanide (A), red., %	-	-	99.0	-	99.2	-	99.5	-
Total solids, mg/L	260,770	130,385	110,000	9,500*	86,600	9,000*	76,2000	8,800*
Total ash, mg/L	242,300	121,150	103,600	8,300*	83,100	8,100*	66,600	7,800*
pH	10.8	-	9.8	-	9.4	-	9.0	-
NH ₃ -N, mg/L	134	67	5,000	-	3,104	-	1,187	-
Sulfide, mg/L	1.36	0.68	-	-	-	-	-	-
Arsenic	<1.2	<1.2	<1.2	<35	<1.2	<35	<1.2	<32
Barium	3.23	1.62	0.017	104	0.012	83.4	0.003	68.0
Cadmium	<0.04	<0.04	<0.004	<1.15	<0.004	<1.15	<0.004	<1.07
Chromium (T)	7.5	3.75	3.24	30.5	3.33	13.5	3.04	13.3
Chromium (+6)	<0.1	<0.1	0.90	IS*	0.66	<3.4	0.18	<3.9
Copper	7663	3832	863	261,440	553	234,600	316	219,450
Lead	0.81	0.40	2.3	464	1.4	229	0.80	172
Mercury	0.0048	0.0024	0.0005	0.23	0.0106	0.14	0.0106	0.153
Nickel	8.46	4.23	0.38	1,305	0.099	408	0.067	337
Selenium	31.2	15.6	13.0	90	9.2	89	5.5	116
Silver	<0.05	<0.05	<0.05	<1.4	<0.05	<1.4	<0.05	<1.3
Zinc	4180	305	305	75,890	159	79,270	29.8	82,565

* Concentrations calculated on 1:1 dilution of raw wastewater.

* Concentration of suspended solids/suspended ash filtered from oxidized waste.

* IS = Insufficient Sample

TABLE 3. WET-AIR-OXIDATION RESULTS FOR F019

Parameter	Autoclave Feed	Oxidized product			
		Filtrate	Cake	Filtrate	Cake
Oxidation temp, °C	-	200	200	240	280
Time at temp, min	-	60	60	60	60
COD, g/L	10.5	1.75	73.7	3.04	2.12
COD reduction, %	-	83.3	-	68	79
pH	8.54	7.95	-	7.9	7.8
NH ₃ -N, mg/L	27.7	527.50	-	668	766
Total solids, g/L*	41.7	2.78	98.8%	2.55	2.08
Total ash, g/L	28.1	1.45	83.9%	1.26	1.35
CN, total, mg/L*	293.1	5.07	22.9 µg/g	0.058	0.133
Total CN from solids, mg/L	-	-	0.91	-	-
Total CN reduction, %	-	98	-	99.9	-
CN amenable, mg/L*	240.9	5	22.9 µg/g	0.02	0.02
Amenable CN from solids, mg/L	-	-	0.91	-	-
Amenable CN reduction, %	-	98	-	>99.9	-
Sulfides, mg/L	<1	<1	-	<1	-
Fluoride, mg/L	38.9	24.7	0.17 µg/g	30.9	38.9
Arsenic, µg/L	80.2	132	114 µg/g	221	<5.0
Antimony, µg/L	<5.0	<5.0	465 µg/g	<5.0	<5.0
Barium, mg/L	2.7	0.21	138 µg/g	0.35	0.77
Beryllium, mg/L	0.007	<0.001	0.32 µg/g	<0.001	<0.01
Cadmium, mg/L	2.11	0.013	102 µg/g	0.007	<0.04
Chromium (T), mg/L	1231	1.92	72,267 µg/g	1.86	24
Copper, mg/L	0.355	0.053	48.7 µg/g	0.046	68,590 µg/g
Iron, mg/L	189	0.13	12,000 µg/g	0.08	34 µg/g
Lead, mg/L	14.7	0.003	816 µg/g	0.008	11,034 µg/g
Mercury, mg/L	0.35	1.1	<0.02 µg/g	1.0	586 µg/g
Nickel, mg/L	0.875	0.007	46 µg/g	0.011	<0.02 µg/g
Selenium, mg/L	50.8	250	<20 µg/g	<5.0	43 mg/g
Silver, mg/L	<0.01	<0.005	<0.5 µg/g	<0.005	<20 µg/g
Thallium, mg/L	<140	9.5	<5 µg/g	5.0	<0.5 µg/g
Vanadium, mg/L	0.31	0.006	<0.5 µg/g	<0.005	<0.5 µg/g
Zinc, mg/L	4902	4.6	61,000 µg/g	4.6	<0.05
					15.2
					279,000 µg/g

* except as noted

PASSIVE TREATMENT OF METALS MINE DRAINAGE
THROUGH USE OF A CONSTRUCTED WETLAND

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ABSTRACT

For contaminant removal, use of a constructed wetland allows one to maximize one or two processes over the many that occur in a natural wetland. For acid mine drainage, anaerobic processes mediated by bacteria will raise the pH and precipitate the heavy metals as sulfides. The Big Five Tunnel Pilot Wetland was built to test these ideas on a metal mine drainage. Since the original construction in 1987 and subsequent modifications in 1988 and 1989, long term removal of contaminants has been achieved and much has been learned about competing removal processes. The best removal efficiency has been with a subsurface flow wetland that is similar to a trickling filter flow system. With this system, 100 % removal of Fe, Cu, and Zn, increase in the pH from below 3 to above 6, and 25 % removal of Mn has been consistently achieved.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

BACKGROUND

Under the SITE Emerging Technology Program, the U. S. environmental Protection Agency is seeking to evaluate and further develop, through pilot scale, promising new technologies for the remediation of Superfund hazardous waste sites. EPA accepted and is jointly funding a proposal from the Colorado School of Mines to evaluate and further develop the technology of constructed (man made) wetlands for treating toxic metals in mineral mine drainage. Ecologists have long understood that soils in wetlands are often foul because they naturally accumulate contaminants. The methods for a wetland to accumulate contaminants include:

1. Filtering of suspended and colloidal material from the water.
2. Uptake of contaminants into the roots and leaves of live plants.
3. Adsorption or exchange of contaminants onto inorganic soil constituents, organic solids, dead plant material, or algal material.
4. Neutralization and precipitation of contaminants through the generation of HCO_3^- and NH_3 by bacterial decay of organic matter.
5. Destruction or precipitation of contaminants in the aerobic zone catalyzed by the activity of bacteria.

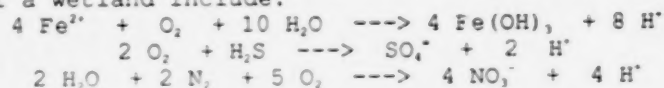
6. Destruction or precipitation of chemicals in the anaerobic zone catalyzed by the activity of bacteria.

With so many possible removal processes, a wetland, such as depicted in Figure 1, is the typical contaminant treatment system in a natural ecosystem. In addition, it operates in a passive mode requiring no additional reactants and no continuous maintenance.

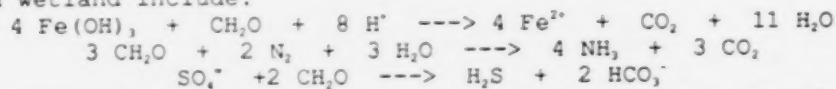
WHY USE A CONSTRUCTED WETLAND?

In the last decade, engineers began to use wetlands for the removal of contaminants from water (1, 2). In some instances, natural wetlands were used. However, a natural system will accommodate all the above removal processes and probably will not operate to maximize a certain process. If a wetland is constructed, it can be designed to maximize a specific process suitable for the removal of certain contaminants from water. Engineering as well as ecological reasons lead to the choice of constructing a wetland for contaminant removal rather than using an existing natural ecosystem.

As an example of constructing a wetland to maximize specific removal processes, consider the bacterial processes that are items 5 and 6 in the above list. Typical microbial mediated reactions that are possible in the aerobic zone of a wetland include:



Typical microbially mediated reactions that are possible in the anaerobic zone of a wetland include:



In these reactions, "CH₂O" is used to symbolize organic material in the substrate.

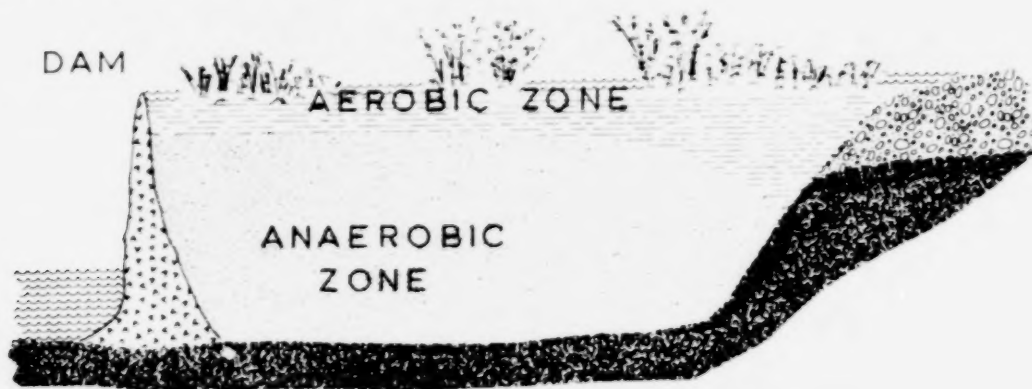


Figure 1. A model of a typical wetland system.

It is apparent that the anaerobic reactions are approximately the reverse of the aerobic reactions. Both zones exist in a wetland. If removal involves aerobic processes, then the wetland should be constructed so the water remains on the surface. If removal involves anaerobic processes, then

the wetland should be constructed so the water courses through the substrate. In a natural wetland, the water primarily remains on the surface. Also, note that the aerobic reactions generate hydrogen ions and the anaerobic reactions consume hydrogen ions.

In the important area of microbially mediated removal, the wetland must be constructed to maximize removal reactions and minimize competing reactions. In the case of removing contaminants from acid mine drainage, it is clear that removal processes should consume hydrogen ions, consequently anaerobic processes are emphasized (3, 4). The research and development at the Big Five Tunnel site in Idaho Springs, Colorado has concentrated on understanding the chemistry and ecology involved in removal and designing structures from readily available materials that maximize these processes.

Although it appears to be "low technology", an intense interdisciplinary effort and creative engineering skills are needed to design and perfect systems that maximize natural processes. For more details on what should be considered, the monographs by Reed, Middlebrooks and Crites (1) and by Hammer (2) are excellent places to begin. For specific information on the use of wetlands for controlling acid mine drainage problems, the U. S. Bureau of Mines Monograph edited by Kleinmann (3) is an excellent source. Note that all three references have been published in the last three years. The technology being considered is still in the development stage.

THE BIG FIVE PILOT WETLAND

ORIGINAL DESIGN, CONSTRUCTION, AND OPERATION

The original design is shown in Figure 2, and construction from that design was completed in the summer and fall of 1987. The completed pilot plant consisted of a 3.05 m wide, 18.3 m long, and 1.22 m deep concrete structure divided into three individual 6.1 m treatment cells (5, 6). The cells were separated from each other by wood walls and each cell was lined with 30 mil Hypalon sheets. The liner isolated each cell and prevented chemical reactions between system components and mine drainage. Mine drainage flowed into each cell at the upstream end through baskets filled with washed 10-to 15-cm river rock. The rock enclosures were about 15 cm long and extended the full width and depth of each cell to facilitate flow through and contact with the substrate. For monitoring purposes, each cell was supplied with a outflow drain at the downstream end and six access wells completed at different depths.

In the original construction, the cells were filled with three feet of the following substrate materials: Cell A - mushroom compost; Cell B - a mixture of equal parts of peat moss, aged manure, and decomposed wood; Cell C - same as B but with a 15 cm layer of 5 - 8 cm limestone rock. From existing wetlands in the region were transplanted cattails (*Typha angustifolia* and *T. latifolia*), sedges (*Carex aquatilis*, and *C. utriculata*), and rushes (*Juncus articus*) into each cell. Each cell was soaked and tested with municipal water for one month and flow of mine drainage through the cells was initiated in October, 1987.

From the beginning, Cell A with mushroom compost was most effective in removing contaminants and raising the pH. Selected values for the mine drainage input and the cell outputs are shown in Table 1. Mn, Fe, Cu, and

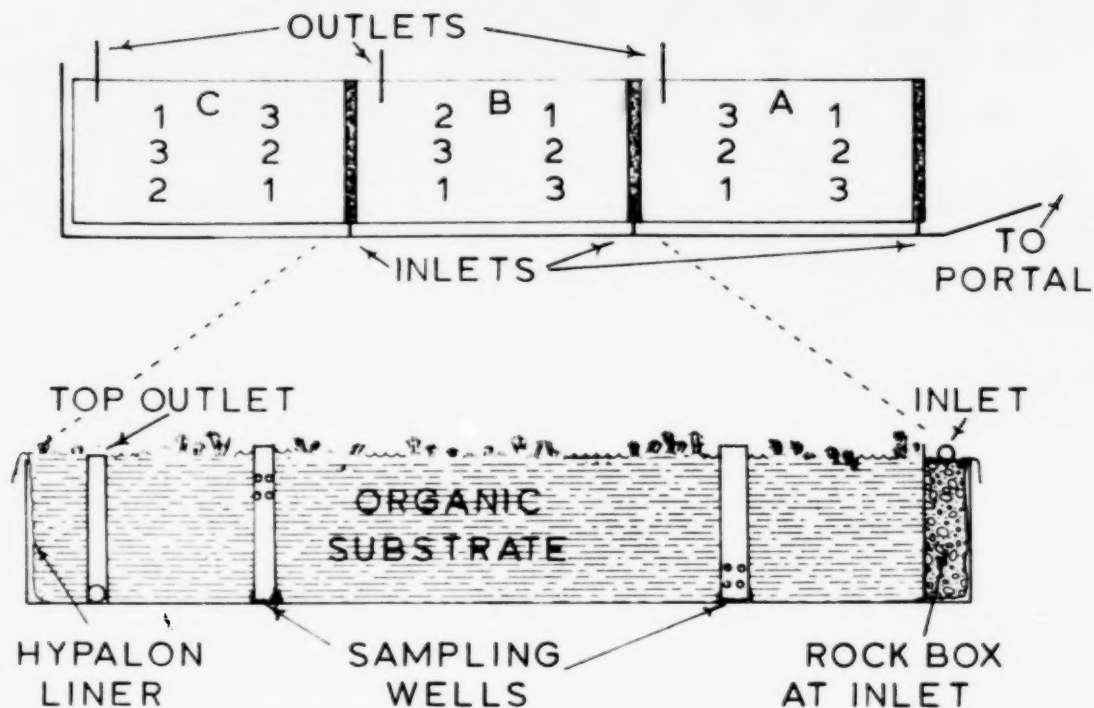


Figure 2. A plan view of the original pilot system at the Big Five Tunnel including an expanded cross section of Cell B.

Zn are the primary heavy metal contaminants and also give excellent indication of the removal processes that are operating (7). It was found that removal strongly depended on the loading rate expressed in square feet/gallon/minute (6). Since the size of the cell is fixed at 18.6 m² (200 ft²), the flow is inversely proportional to the loading rate. The best results for Cell A during this period were 100 % removal of Cu and Zn, 63 % removal of Fe, and an increase in pH from 3.0 to 6.2 at a loading rate of 600 ft²/gal/min. In the first stage of operations, Mn was not removed. The removal patterns and results from other experiments performed on the substrates (7, 8) gave convincing evidence that the important removal process was bacterial reduction of sulfate in the mine drainage to hydrogen sulfide and subsequent precipitation of the metals as sulfides.

PROBLEMS WITH THE ORIGINAL DESIGN

In acid mine drainage, Fe (II) is continuously oxidizing and precipitating as Fe(OH), (4). Many of the problems encountered during original operation were attributed to clogging by ferric hydroxides (6). Pipes, valves, and rock baskets all became clogged and maintenance frustrated the objective of passive operation. Also, when it was realized that the important removal processes were occurring in the substrate anaerobic zone, the original design appeared inadequate for maximizing contact of water with substrate. Figure 2 shows that water flows out from the top of the cell and this insures a poor flow pattern through the anaerobic zone. Subsequent phases of the project involved the redesign and construction of cells to maximize contact and subsurface flow.

TABLE 1. CONCENTRATIONS (mg/L) OF METALS, PERCENT REDUCTION OF METALS, pH, AND FLOW RATES (GALLON/MINUTE) IN THE BIG FIVE MINE DRAINAGE AND WETLAND CELL OUTPUT WATERS.*

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
=====										
INITIAL OPERATION										
December 11, 1987										
Mine Drainage	34		32		10.6		1.02		2.8	
Cell A	27	21	18	45	7.8	27	0.44	57	4.6	1.0
Cell B	33	1	24	26	9.8	12	0.89	12	3.1	1.0
Cell C	34	0	22	32	9.6	9	0.91	10	3.3	1.0
August 19, 1988										
Mine Drainage	26		37		8.1		0.91		2.9	
Cell A	25	4	20	56	<0.1	100	0.17	81	5.5	0.51
Cell B	26	0	15	59	6.1	24	0.55	40	3.2	0.24
Cell C	25	4	11	70	5.8	28	0.38	58	3.5	0.34
CELL A MODIFICATION										
February 21, 1989										
Mine Drainage	27		32		9.3		0.56		3.0	
Cell A	22	19	12	63	4.5	52	<.05	100	5.1	0.28
Cell B	27	0	28	13	6.1	34	0.82	0	3.4	0.31
Cell C	25	7	31	3	7.2	23	0.26	53	3.5	0.32
May 6, 1989										
Mine Drainage	30		42		10.4		0.76		3.0	
Cell A	33	-10	28	33	7.8	25	<.05	100	3.5	0.92
Cell B	27	10	10	76	6.2	40	0.36	53	3.0	0.83
Cell C	29	3	9	79	6.4	38	0.46	39	3.2	0.81
August 1, 1989										
Mine Drainage	32		43		9.4		0.75		2.9	
Cell A	31	3	39	9	5.2	45	<.05	100	4.1	0.30
Cell B	26	19	24	44	6.6	30	0.46	39	3.1	0.48
Cell C	32	0	18	58	4.8	48	0.09	88	3.7	0.43
CELL B MODIFICATION										
October 3, 1989										
Mine Drainage	35		46		9.9		0.66		3.2	
Cell B-Up	34	3	39	15	9.3	6	0.59	11	3.5	0.29
Cell B-Down	23	34	8	83	0.8	92	<.05	100	6.5	0.16
Cell E	24	31	<1	100	<0.1	100	<.05	100	6.3	0.062
November 5, 1989										
Mine Drainage	32		38		8.7		0.61		2.9	
Cell B-Up	31	3	17	55	8.4	3	0.48	21	3.6	0.22
Cell B-Down	20	38	<1	100	6.0	31	<.05	100	5.9	0.24
Cell E	20	38	<1	100	<.1	100	<.05	100	6.5	0.11
January 13, 1990										
Mine Drainage	31		33		9.0		0.59		2.9	
Cell B-Up	30	3	33	0	8.9	1	0.49	17	3.2	0.21
Cell B-Down	27	13	12	64	8.1	10	0.44	25	3.2	0.20
Cell E	28	10	10	70	<.1	100	<.05	100	6.0	0.10

*The area of Cells A, B, and C is 200 ft²; the area of Cells B-Up, B-Down, and E is 100 ft².

SUBSEQUENT MODIFICATIONS

CELL A MODIFICATION

The first redesign concentrated on the issue of increasing the contact of the drainage with the substrate especially in the anaerobic zone. This was accomplished by the addition of: Two walls running the length of the cell to increase the flow path length by a factor of three, and six redistribution baffles to collect water flow from the top surface and redistribute it to the bottom of the substrate. This was done on Cell A and a cut-a-way view of the redesign is shown in Figure 3. Essentially, Cell A was redesigned to be a six segment plug flow reactor (9).

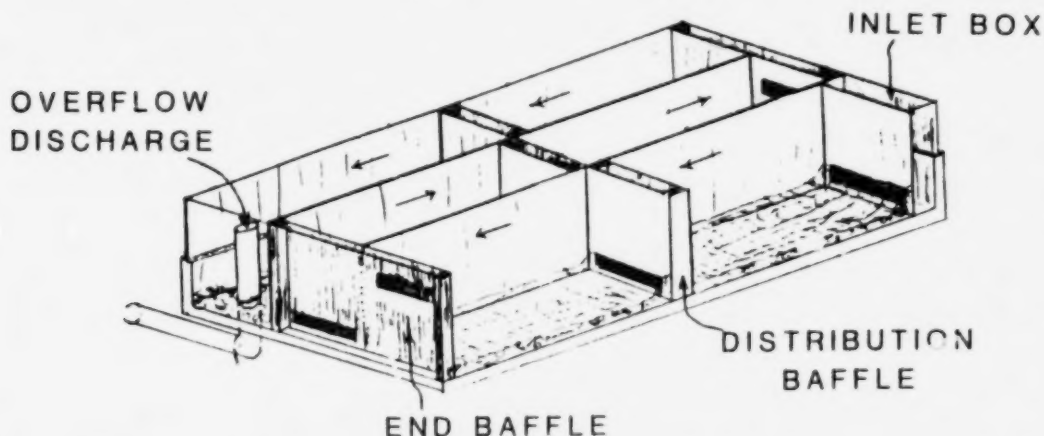


Figure 3. A cut-a-way view of the modification done to Cell A.

Although the initial structure design was amenable to major changes, the results of the redesign were discouraging. The desired plug flow from segment to segment through the lower part of the substrate was not achieved. Considerable water flowed across the top of cell segments and leaked from one segment to others. When the cell was modified, the original mushroom compost was removed, stockpiled, and returned to the cell after the remodeling. It was speculated that through this handling, substrate permeability significantly decreased. Subsequent experiments on new and used mushroom compost verified that permeability decreased from 3.0×10^{-3} to 9.2×10^{-5} cm/sec (10). Selected values on removal and changes in pH from the cells during this phase are shown in Table 1.

As a result of this setback, a laboratory and bench scale program was developed to determine how well typical soil tests could be adapted to this highly organic substrate. Especially important were the development of methods to determine hydraulic conductivity that could give reasonable indications of what to expect in a constructed wetland (10). Other tests on substrates included the determination of specific gravity, bulk density, size fractions, and percent moisture.

CELL B MODIFICATION

Results of laboratory and bench-scale permeability experiments led to the modification of Cell B into upflow and downflow cells to monitor and

evaluate permeability at the pilot scale. The original cell was divided into two lined, identical cells so individual variables could be tested. All features needed to determine soil permeability in the cell were included. A special feature in the design was inclusion of a plenum beneath each subcell for even distribution of drainage in the upflow configuration and even collection when used as a down flow cell. Each cell could be operated in the upflow or downflow configuration. Figure 4 is a cut-a-way diagram of the downflow operation.

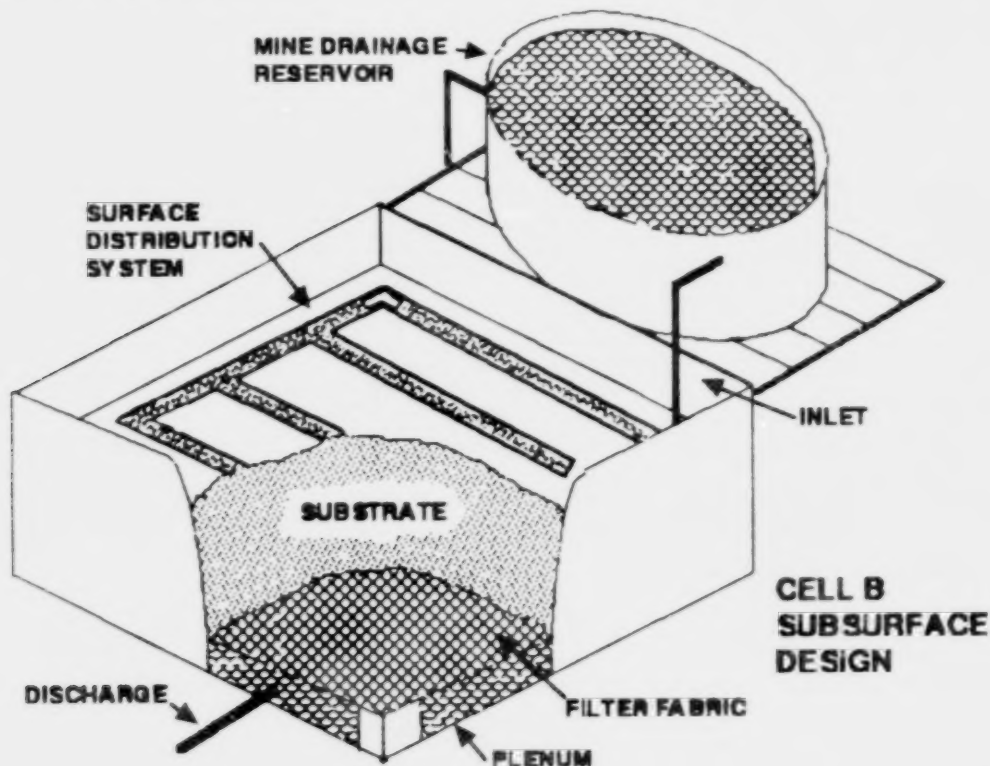


Figure 4. A cut-a-way view of the modification done to Cell B. Two identical subcells were constructed; figure shows a downflow configuration.

There are a number of features in this modification that should improve contact with the substrate. When operating either as an upflow or downflow cell, the mine drainage is forced through the substrate before discharge. This configuration is comparable to a trickling filter process instead of the plug-flow reactor design in the Cell A modification (9). Also included in the modification, was the addition in series of two 150-gallon stock tanks before the inlets of the subcells. Figure 4 shows the placement of one of the tanks. The tanks serve the purpose of completing the precipitation of ferric hydroxides before drainage enters the subcells so that plumbing, plenums, and filter fabrics do not become clogged.

Remodeling of Cell B was completed in August, 1989. The two subcells were filled with fresh mushroom compost to a depth of 0.61 m. Flow of mine drainage through the subcells was initiated on September 1. One subcell was operated in the upflow configuration, the other downflow. Upflow

permeability measured 1.3×10^{-3} cm/sec, and downflow permeability measured 3.1×10^{-4} cm/sec (10). The development of laboratory and bench-scale methods for predicting permeability in actual constructed wetlands has proven successful.

Values on removal of Mn, Fe, Cu, and Zn and increases in pH for Cell B-Upflow and Cell B-Downflow are given in Table 1. Just as for the original Cell A design, removal has been impressive from initiation of flow. Removal from the downflow system is better than from the upflow, however, flows through the cells have not always been equal so a true comparison has yet not been completed. After 3 months, removal is not as good as during the first month. Recent laboratory studies on the substrate have shown that the complexing of metals onto organic sites in the substrate can occur and that this is a significant removal process at the start-up of a constructed wetland (6). Even so, the Cell B-Downflow appears to be operating better than Cell A at comparable loading factors.

CELLS D AND E DESIGN, CONSTRUCTION, AND OPERATION

When Cell B was remodeled, Cells D and E were constructed using the original substrate from Cell B. Cell D was designed to polish discharges from anaerobic cells by using aerobic processes. Features of the design include a shallow depth (0.50 m) and a length to width ratio of 10. It has been receiving the discharge from Cell A and removal of Cu, Zn, and Fe is completed and the pH is raised to above 6.

Cell E was designed to operate as a downflow, subsurface wetland. Construction was completely accomplished with materials found locally. It is approximately 9.3 m² and the substrate is 0.61 m deep. Subsurface flow is achieved by flow through landscape fabric into 2.5-cm gravel and subsequent discharge into a tube on the downflow end. For this system, results have been excellent.

Flow of mine drainage through Cell E was initiated on September 1, 1989. From the beginning, removal of Cu, Zn, and Fe has been 100 %, pH has increased to 6.5, and Mn removal has averaged 25 %. Removal results are given in Table 1 and are shown in Figure 5. Laboratory experiments have confirmed that sulfate reduction with subsequent precipitation of metal sulfides is the predominant removal process in Cell E (7).

ADDITIONAL CONSIDERATIONS

A possible toxic metal removal mechanism would be through accumulation in leaves, stems, and roots of wetland plants. Should this occur, it could create problems by concentrating toxic metals in the biologically very active wetland surface. However, at the Big Five Site, careful collection and analysis of wetland plant samples has revealed only minor accumulation of toxic metals after two years of operation. This result is consistent with studies of wetland removal systems used for coal mine drainage that show that uptake by plants accounts for at most 5 % of the metal removal (11).

Gradually over considerable time, toxic metals will accumulate in the anaerobic and aerobic zones of a wetland. At some point, these metal sulfides and hydroxides mixed with organic substrate will have to be removed from the wetland and treated for disposal or be recycled for metal recovery. However, the quantity of sludge to be thus handled represents a small

fraction of that which would be produced by more conventional processes and this sludge may even have economic potential for metal recovery.

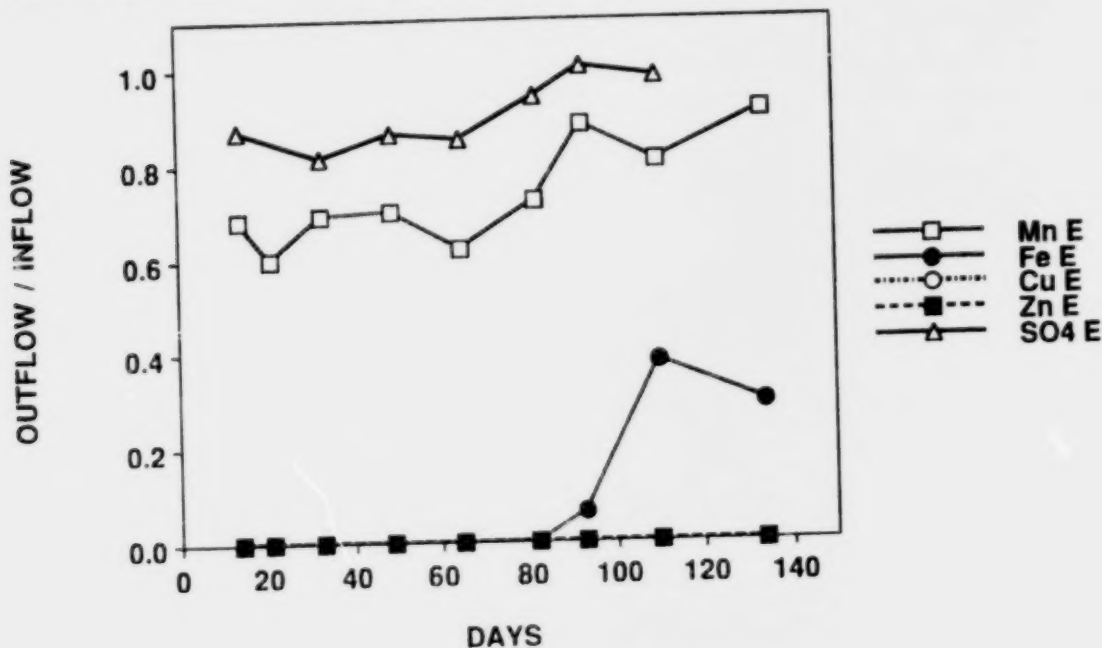


Figure 5. Cell E removal data since September 1, 1989.

CONCLUSIONS

Using constructed wetlands for wastewater treatment is still a developing technology. However, the results from the Big Five Pilot Wetland that was funded by the Emerging Technology Program (ETP) of the U. S. EPA shows promising removal of heavy metals and increase of pH for acid mine drainage. Conclusions from the project include:

1. Toxic metals such as Cu and Zn can be removed and the pH of mine drainage can be increased on a long term basis.
2. The major removal process is sulfate reduction and subsequent precipitation of the metals as sulfides. Exchange of metals onto organic matter can be important during the initial period of operation.
3. A trickling filter type of configuration achieves the best contact of the water with the substrate.
4. Removal efficiency depends strongly on loading factors. In the Big Five wetland, factors above 1,000 feet³ per gallon/minute are needed for reasonable removal.
5. Permeability of the substrate is a critical design variable for successful operation. Using laboratory and bench-scale tests, a good indication of the soil permeability in a constructed wetland can be determined.
6. Solutions to problems such as plugging of plumbing by ferric hydroxides and freezing of discharge lines during winter have to be designed and constructed into the passive nature of wetlands to achieve long term operation.

7. Eventual removal of precipitated metal sulfides for metal recovery or disposal must be included in the operating plan.

ACKNOWLEDGEMENTS

Development of environmental technology doesn't occur without scientists and engineers taking an interdisciplinary approach and sponsors taking risks. For this project, success required many people to see the broad picture and take risks. Among them are: Roger Olsen and Richard Chappell of Camp, Dresser, and McKee; John Gormley and James Gusek of Denver, Knight, Piesold; Holly Fliniau, James Kreissl, and James Lazorchek of the U. S. EPA; and Jeff Deckler and Jeb Love of the Colorado Department of Health.

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SOIL VAPOR EXTRACTION TECHNOLOGY ASSESSMENT

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ABSTRACT

Soil vapor extraction (SVE) systems are being used in increasing numbers due to many advantages these systems hold over other soil treatment technologies. SVE systems appear to be simple in design and operation, yet the fundamentals governing subsurface vapor transport are quite complex.

In view of this complexity, an expert workshop was held to discuss the state-of-the-art of the technology, the best approach to optimize system application, and process efficiency and limitations. As a result of the workshop, an SVE Technology Assessment report was produced. This report discusses the basic science of the subsurface environment and subsurface vapor flow, site investigations, SVE system design and operation, monitoring, emission control, and costs. The report also serves as the proceedings of the expert workshop. Additional research activities being conducted include a field demonstration of a structured SVE system design approach; a laboratory column study to determine and characterize residuals following vapor extraction; an assessment of secondary emissions and regulations governing releases from SVE systems; cost of SVE implementation and operation; and a survey of techniques to enhance vapor removal.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Soil vapor extraction (SVE) is being used with increasing frequency at sites throughout the country for the remediation of unsaturated zone soils that have become contaminated with volatile organics. SVE, also known by various names such as vacuum extraction, in situ vaporization, or soil venting, has many positive features that give it an advantage over other

soil treatment techniques such as excavation and off-site treatment, soil flushing, or biotreatment. Some of the features that make this technology applicable to a broad spectrum of sites are:

- o SVE is an in situ technology, so there is a minimum of site disturbance; often, business operations at the site need not be interrupted;
- o SVE can treat large volumes of soil at reasonable costs;
- o SVE is easily installed and uses standard, readily-available equipment, which allows for rapid mobilization and implementation of remedial activities;
- o SVE is effective in reducing the concentration of volatile organic compounds (VOCs) in the vadose zone, reducing the potential for further migration; and
- o SVE complements groundwater pump and treat techniques, which may be instituted concurrently.

These features, combined with the apparent simplicity of SVE system design, implementation, and operation, have combined to make SVE systems one of the fastest growing remediation choices. This growth has not necessarily been accompanied by a concomitant expansion of the knowledge base to design and operate an SVE system properly. Indeed, the ease with which SVE systems can be installed and operated belies the very complex nature of subsurface vapor behavior and transport.

Much of the technical information regarding the design, construction and operation of an extraction system is held by the SVE technology developers and vendors. Engineering practices, which are often considered proprietary by the developers and vendors, may be based in large part on each developer's experiences. This atmosphere does not encourage rigorous objective review of design or operating methods and makes it more difficult to analyze the results of SVE use. Some vendors claim complete remediation of a site to a specified level, yet are reluctant to share their methods or procedures used to determine attainment of those goals. This lack of knowledge poses limitation to regulatory agency personnel or others trying to interpret system operating results.

It was recognized that gaining a deeper understanding of various aspects of soil vapor behavior would help researchers, vendors, consulting engineers, and regulatory agency personnel. It was the increased use of these systems and the need for a greater understanding of the principles that underlie soil vapor behavior and other issues related to SVE that led ORD, through its Risk Reduction Engineering Laboratory, Release Control Branch (RREL-RCB) to initiate SVE research efforts. This paper discusses the activities thus far, summarizes the results, and highlights the upcoming research to be completed under this contract.

WORKSHOP

The initial step in these efforts was the convening of an expert workshop in Edison, NJ on June 28 and 29, 1989. Workshop participants included SVE technology vendors, petroleum industry representatives, university researchers, consulting engineers, regulatory agency representatives, and others who were familiar with this technology. The workshop had dual objectives. One goal was to discuss the state of the art of SVE related topics, such as site characterization, SVE pilot systems, full scale system design and operation, vapor treatment options, the setting and attainment of cleanup criteria, and monitoring of SVE progress. Some presenters discussed actual case studies; others discussed a structured framework for conducting site investigations and system design, the use of modeling to help design extraction systems, and other research on SVE currently in progress. The second objective of the workshop was to discuss additional research needs. Panel discussions were held with workshop attendees regarding areas for future research and topics needing immediate attention. The regulatory climate was also discussed, including suggested remediation standards and methods to determine cleanup attainment.

The consensus of those present was that SVE is effective for removing a wide range of volatile compounds. Hutzler et al. (1988) reported the results of an extensive survey of operating SVE systems. Data reported included number and type of wells, well spacing and rate of influence, type of pumps and auxiliary equipment used. These reports showed that, while SVE was very often successful in removing volatile contaminants, many times this technique was used without a complete understanding of the physics and chemistry behind the process.

SVE TECHNOLOGY ASSESSMENT DOCUMENT

The SVE Technology Assessment Report was produced based on the information presented at the workshop and subsequent research efforts. This two-part report contains sections on the principles of soil vapor behavior; the performance of site investigations prior to SVE use; SVE system design approaches; system operation; system monitoring; vapor treatment and cost in Part 1. Part 2 of the report serves as the proceedings to the expert workshop and contains selected papers presented at the workshop. Papers were selected to provide coverage representative of the wide range of topics discussed. The report was written for an audience that desires an in-depth understanding of the soil vapor extraction and treatment process. A summary of the findings presented in this document is presented below.

PRINCIPLES OF SOIL VAPOR BEHAVIOR

Products released into the subsurface environment from UST systems are acted upon by numerous forces that influence the degree and rate at which they migrate from the source. The extent to which the released products partition into the vapor phase is dependent upon the characteristics of the

product, the soil environment, and the elapsed time since the release occurred. The manner in which the release product behaves in the subsurface will have a significant bearing on whether soil vapor extraction could be an approach for the site under consideration. Figure 1 is a nomograph that uses vapor pressure and soil air permeability (with the length of time since release) to show the applicability of SVE.

Contaminant Characteristics

The physical and chemical properties of the released product control, to a great extent, the movement and ultimate fate of that product in the subsurface. The degree to which a compound partitions into the vapor phase is described by that compound's vapor pressure and Henry's law constant. The soil sorption coefficient, K_d , describes the tendency of a compound to become adsorbed to soil. The solubility describes the degree to which a product will dissolve into pore water. The distribution of a product among the three phases will vary with changes in site-specific conditions and will also change over time in response to weathering.

The released product's volatility controls in large part the quantity present as vapor in the soil pores. Volatility is perhaps the most important product characteristic affecting applicability of soil vapor extraction to that compound. The parameter that best describes a compound's volatility is its vapor pressure.

Vapor Pressure--

Vapor pressure is the force exerted by the vapor of the chemical in equilibrium with its pure solid or liquid form. Generally, compounds with vapor pressures of less than 10^{-3} mmHg are not volatile and are not removed by SVE (Dragun, 1988); vapor pressures above 0.5 mmHg are removed to a significant degree (Bennedsen et al., 1985). Many gasoline constituents have sufficiently high vapor pressures that they can be removed by SVE (Table 1).

Henry's Law--

Henry's law governs the volatilization from a contaminant in solution, rather than from a pure product. Henry's law constant (K_h) may be a more appropriate partitioning constant outside of the free product zone, where product is likely to exist in solution with pore water (Stephanatos, 1988). Compounds with K_h above 0.01 (dimensionless) are suitably volatile for removal via SVE (Hutzler et al. 1989). Gasoline, with a composite $K_h=32$, is particularly well-suited to SVE.

Soil Sorption Coefficient--

Sorption of contaminant to soil particles and organic matter controls the distribution of released products in the soil zone and has a very strong effect on the movement of the product through the vadose zone. In many cases the majority of the released product may exist in the sorbed phase. A strong relationship exists between the organic carbon content of the soil and the sorption coefficient. As soil organic carbon content increases, the sorption for most products increases.

Water Solubility--

Solubility controls the degree to which a product dissolves into groundwater and pore water present in the vadose zone. Soluble products are more likely to dissolve in infiltrating precipitation and move away from the source.

Contaminant Composition--

Petroleum hydrocarbons, the most common products released from underground storage tanks (EPA, 1988), are actually mixtures of many different compounds. Each particular type of petroleum product has a different composition and therefore will behave differently in the subsurface. SVE is more applicable to those mixtures with greater amounts of lighter end fractions (e.g., gasoline) versus heavier-end fractions (e.g., diesel or heating oils).

Weathering--

Weathering refers to the changes in the nature of a chemical mixture after its release into the environment. The product composition will change over time and affect the ease with which that product may be removed via SVE. The more volatile, soluble, and degradable compounds will be removed from the mixture, leaving the resultant mixture relatively richer in less-volatile, less-soluble, and more-refractory compounds. Figure 2 shows the composition by class for gasoline. Weathering has applicability to SVE because this phenomenon also occurs as SVE progresses, as the more volatile fractions are removed. Figure 3 shows the change in composition of extracted vapor at a site in Utah (DePaoli et al., 1989). As SVE proceeds, the extracted vapors are progressively enriched with heavier compound.

Soil Environment

Similar to the product characteristics, the soil environment significantly affects the transport and fate of released products and the likelihood of success with SVE. The most important properties are summarized below.

Soil structure--

Coarse-textured, highly permeable soils are best suited to SVE. SVE has also worked successfully, however, in clays and silts, where interbedded permeable layers exist or macroporosity and secondary structure exist.

Air permeability--

The air permeability of the soil is perhaps the single most important soil parameter with respect to the success of vapor extraction. The permeability incorporates the effects of several soil and vapor characteristics. The more important soil characteristics are the stratigraphy, air-filled porosity, particle size distribution, water content, residual saturation, and the presence or absence of macropores or

preferred flowpaths; important product characteristics include the vapor viscosity and vapor density.

Soil water content has a significant effect on the air permeability. In general, higher water contents reduce the air-filled porosity thereby decreasing the connected pores through which air can flow by advection.

Ganglia formation--

Ganglia, or isolated globules of product that remain in soil micropores, may form in soils with fissures, cracks, or other dead end pores. A high degree of ganglia formation retards SVE suitability.

Water content--

SVE is generally more successful at lower moisture contents. High water content reduces the air-filled porosity, with a reduction in air permeability (Figure 4). If the water content is very low, however, sorption force to soil increases, leading to reduced volatilization into the soil gas (Reible, 1989). A range of 94 to 98.5 percent relative humidity in soil gas appears to be optimal for SVE (Davies, 1989).

Vapor Transport

Darcy's law is typically used to describe vapor flow through soils. Under vacuum conditions, the applied gradients dominate the natural gradients, and the law simplifies to:

$$q_a = (K_a / n_a) \nabla P_a$$

where

- q_a = volume flow per unit area
- K_a = air permeability of the soil
- n_a = air viscosity
- P_a = applied vacuum

Obviously, the air permeability plays a key role in determining SVE applicability and also in system design. The air permeability incorporates many soil characteristics including porosity, structure, grain size distribution, water content, and preferred flow paths. Other things being equal, SVE applicability is a function of air permeability.

SITE INVESTIGATIONS

The initial step in considering remediation for a site is the performance of a site investigation, including a site history review, preliminary site screening, detailed site screening, and contaminant assessment.

During a site history review, all the available information that may be useful is assimilated. Typically, this information will include reports, maps, and other data. Sources for this information often include federal agencies such as EPA, USGS, SCS, FEMA, and state and local agencies.

Preliminary site screenings consist of a site visit, limited sampling (often soil gas surveys), and the development of a site map. The main objective is to delineate the extent of contamination. Equipment used often includes soil gas survey equipment, and a PID, FID, or gas chromatograph (GC).

A detailed site characterization is performed to obtain data needed for SVE system design. Data obtained usually include air permeability, moisture content, soil type and structure, and other data. Typically, this step would include borings, geophysical techniques, and monitoring well installation.

Soil vapor contaminants are normally characterized via soil GC analysis. This step also helps to determine potential SVE effectiveness and may be of value to set cleanup goals.

Pilot testing is performed to allow for the determination of specific soil and contaminant properties that will be used in full-scale system design.

SYSTEM DESIGN

SVE systems are designed to maximize the air flow through the zone of contamination. Vertical wells, trenches or soil piles may be used as extraction points. Wells are used where contamination exists at depth, while trenches are more appropriate where the water table is near the surface. Contaminants may also be removed from stockpiled soil, which may result when soil is excavated from around a leaking tank.

The radius of influence of the extraction well is the primary design variable. The radius, which is determined by the results of a site-specific air permeability test or during pilot studies, depends most highly on the applied vacuum and the air permeability of the soil (Figure 5). The radius of influence can also be affected by the depth to water, the position of the extraction vents relative to the surface, or the presence of an impermeable surface seal. Air inlet or injection wells are also used to control the radius of influence. Inlet wells allow air to enter the subsurface at specific points, while injection wells force air into the soil. Ground water depression pumps may be used with SVE systems to reduce ground water upwelling.

EQUIPMENT

Most systems contain piping, a vacuum pump or positive displacement blower as the motive force, vapor pretreatment (air/water separator), and emission control (Figure 6). The piping is typically PVC, with the diameter varying with the design air flow. Both blowers and vacuum pumps are used. Air-water separators can be as simple as a 55-gallon drum or may include refrigerated condenser units, demisters, level controls, and other devices. Emission control may be accomplished using granular activated carbon, incineration, or catalytic oxidation. Internal combustion engines and biotreatment have also proved successful.

SYSTEM OPERATION AND MONITORING

SVE can be operated automatically and controlled via microprocessors, or can be operated manually. Cleanup progress is assessed by volume flow rate and vapor concentration monitoring. These data are normally converted to a mass flow rate. Extraction may be continuous or "pulsed" (i.e., intermittent). Pulsed venting may be more energy-efficient.

Monitoring of vapor phase concentration and composition in extracted vapors is done on a regular basis. The data collected are used to show the progress made by SVE. Monitoring typically shows that removal rates drop as the cleanup progresses, as the most volatile compounds are removed first.

SVE has also been shown to enhance levels of biotreatment in soils, probably due to the inflow of added oxygen. DePaoli et al. (1989) calculated that 27.5% of total removal at one site was due to biodegradation.

SECONDARY EMISSIONS CONTROL

There are four common options for treating the vapors removed from the soil by SVE: granular activated carbon (GAC) adsorption, incineration, catalytic oxidation, and internal combustion engines (ICEs). Each method has advantages and disadvantages, and no single method is most appropriate for all situations.

Granular Activated Carbon (GAC)

GAC is the most common treatment method for vapors, for various reasons, including familiarity, ease of implementation and operation, possibility of regeneration, and its applicability to a wide range of contaminants, concentrations and flowrates. GAC generally may not be the most cost-effective option where mass removal rates are high, due to the increased costs of carbon regeneration or replacement.

Incineration

Incineration uses very high temperatures (1400°F or higher) to destroy vapor phase contaminants. This method is good for streams with high concentrations, since the incineration can become self-sustaining at vapor concentrations over about 10,000 ppmv. Below this level, supplemental fuel must be used.

Catalytic Oxidation

Catalytic oxidation employs a precious metal formulation as a catalyst, allowing the reaction to occur at temperatures of 800°F, significantly below the temperature needed for incineration. This results in reduced fuel costs. The incoming vapor stream concentration is limited to about 3000 ppmv, because at concentrations above this level the heat of combustion will destroy the catalyst. These units are not suited for use in chlorinated vapor streams due to potential catalyst degradation.

Internal Combustion Engines

In southern California, over 100 internal combustion engine systems have been permitted for use at SVE sites. Results show the units provide good reduction in hydrocarbon concentrations (>99%). These units are composed of an automobile engine with a carburetor modified to accept vapor phase fuel.

COSTS

The costs of SVE may be divided into site investigation, capital, operation and maintenance, and monitoring costs.

Site investigation costs include those associated with gathering site historical data, performing a preliminary site characterization, and, if needed, a detailed site characterization and contaminant assessment. For a typical leaking UST site like a gasoline service station, the site investigation phase may be limited in scope and cost.

Capital costs include the costs of procuring and installing all equipment, piping, and instrumentation necessary for system operation. Engineering costs are also usually included in this category. Major cost factors are typically the well drilling and installation, the blowers, and the emission control system, if needed. Fully-contained units are now available for purchase or lease.

Operation and maintenance costs consist chiefly of power for the blowers and pumps and costs associated with the emission control system. Emission control units, typically incinerators or granular activated carbon, can dominate the cost of SVE. Monitoring costs include laboratory and field analytical costs such as gas chromatograph analysis, which is used to determine the efficacy of the SVE system and/or cleanup attainment.

Typical costs for a complete installation may vary over a wide range, from as little as \$10,000 for a small site to well over \$1,000,000 for a large, multi-acre site. Gasoline service stations may be cleaned for under \$100,000 in some cases. On a unit basis, reported costs have ranged from \$10/yd³ to over \$300/yd³, with lower costs associated with larger sites.

CONCLUSIONS

Soil vapor extraction systems are being used in increasing numbers for the removal of volatile organic compounds from unsaturated zone soils. These systems operate in situ, so there is a minimum of site disturbance and site operations need not be interrupted; they can treat large volumes of soil at reasonable costs; and are relatively easy to install, allowing for rapid mobilization and implementation. Although these systems appear to be simple, however, subsurface vapor flow is quite complex.

A workshop was held to discuss the state-of-the-art of the technology. Based on the workshop and subsequent research, an SVE Technology Assessment report was produced, which discusses basic science of the subsurface

environment, subsurface vapor flow, SVE system design and operation, secondary emission control, and costs.

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TABLE 1. CHEMICAL PROPERTIES OF HYDROCARBON CONSTITUENTS

Chemical Class	Representative Chemical	Liquid Density (g/cm ³) @ 20°C	Henry's Law Constant (dim.)	Water solubility (mg/L) @ 25°C	Pure Vapor Pressure (mm Hg) @ 20°C	Vapor Density (g/m ³) @ 20°C	Soil Sorption Constant (Koc) (L/kg) @ 25°C
<u>n-Alkanes</u>							
C4	n-Butane	0.579	25.22	61.1	1560	4960	250
C5	n-Pentane	0.626	29.77	41.2	424	1670	320
C6	n-Hexane	0.659	36.61	12.5	121	570	600
C7	n-Heptane	0.684	44.60	2.88	35.6	195	1300
C8	n-Octane	0.703	52.00	0.86	10.5	65.6	2600
C9	n-Nonane	0.718	NA	0.122	3.2	22.4	5800
C10	n-Decane	0.730	NA	0.022	0.95	7.4	13000
<u>Mono-aromatics</u>							
C6	Benzene	0.885	0.11	1780	75.2	321	38
C7	Toluene	0.867	0.13	515	21.8	110	90
C8	m-Xylene	0.864	0.12	162	8.16	35.6	220
C8	Ethylbenzene	0.867	0.14	167	7.08	41.1	210
C9	1,3,5-Trimethylbenzene	0.865	0.09	72.8	1.73	11.4	390
C10	1,4-Diethylbenzene	0.862	0.19	15	0.897	5.12	1100
<u>Phenols</u>							
Phenol	Phenol	1.058	0.038	82000	0.529	2.72	110
C1-phenols	m-Cresol	1.027	0.044	23500	0.15	0.89	8.4
C2-phenols	2,4-Dimethylphenol	0.965	0.048	1600	0.056	0.39	NA
C3-phenols	2,4,6-Trimethylphenol	NA	NA	NA	0.012	0.09	NA
C4-phenols	m-Ethylphenol	1.037	NA	NA	0.06	0.53	NA
Indanol	Indanol	NA	NA	NA	0.014	0.1	NA
<u>Diaromatics</u>	Naphthalene	1.025	NA	30	0.053	0.37	690

NOTE: NA - Not available

SOURCE: Compiled from various published and unpublished sources.

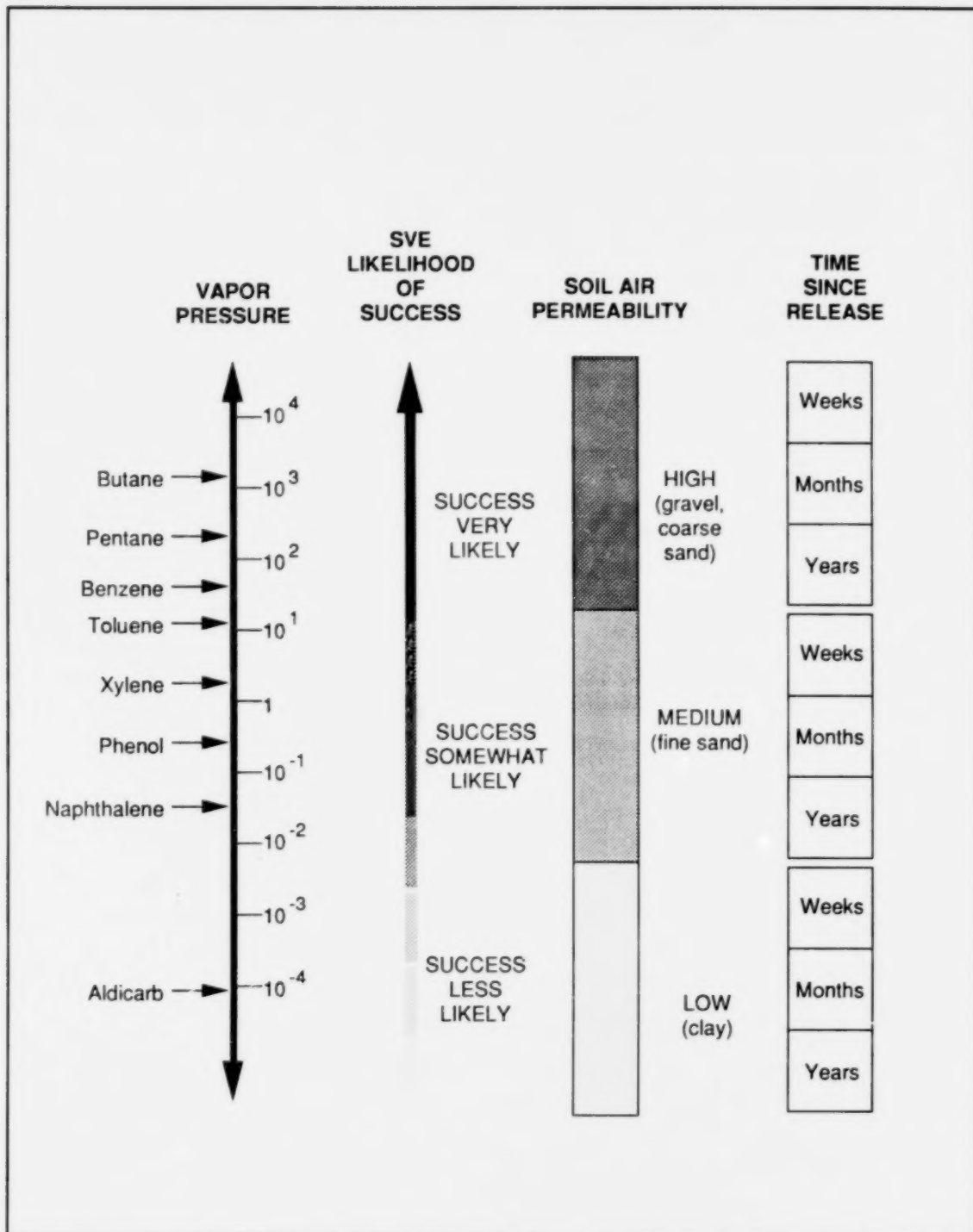


Figure 1. SVE Applicability Nomograph

COMPOSITION OF GASOLINE

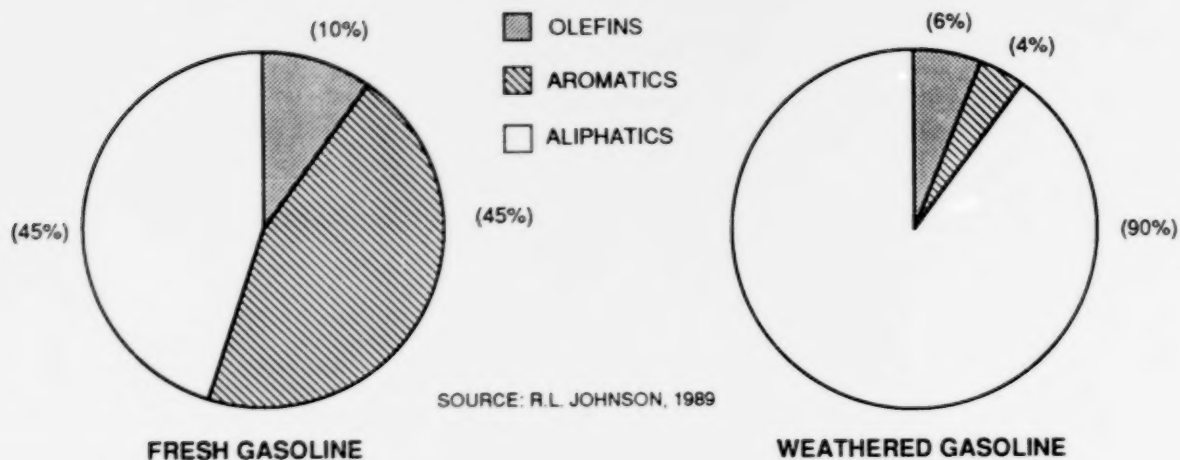


Figure 2. Effect of Weathering on Gasoline Composition

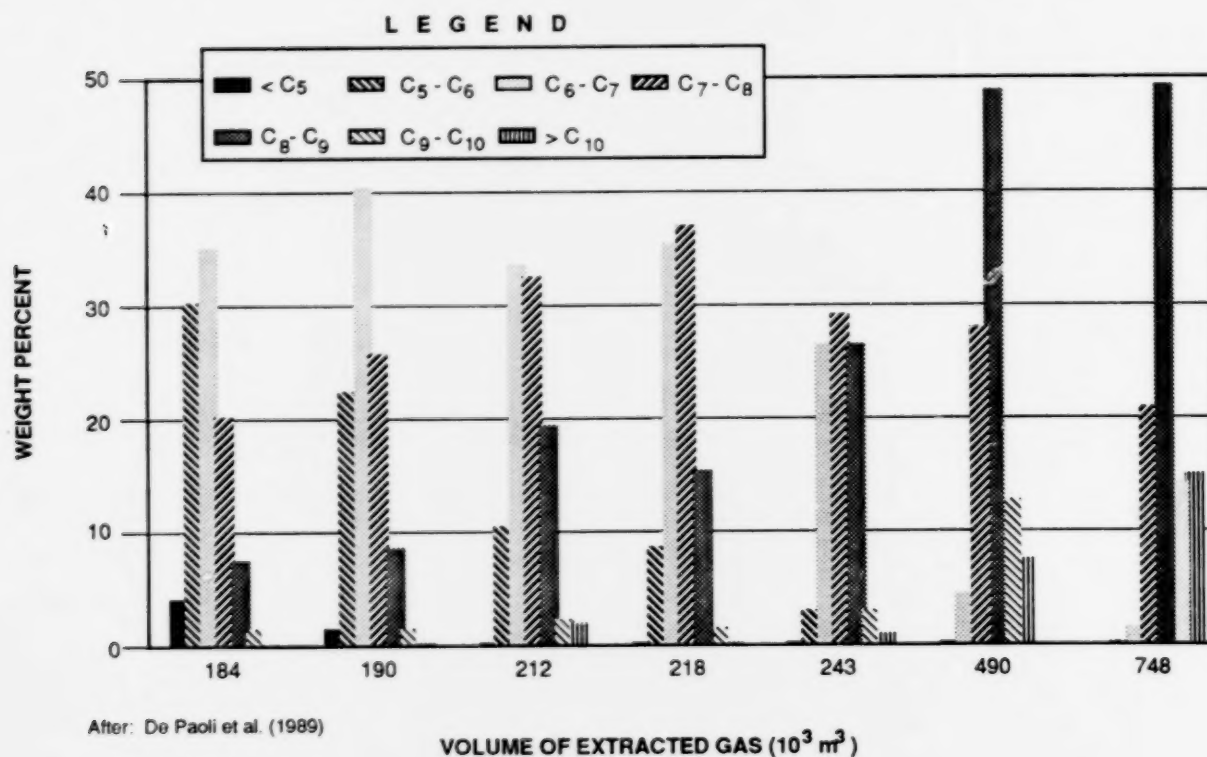


Figure 3. Variation of Hydrocarbon Distribution in Extracted Gas

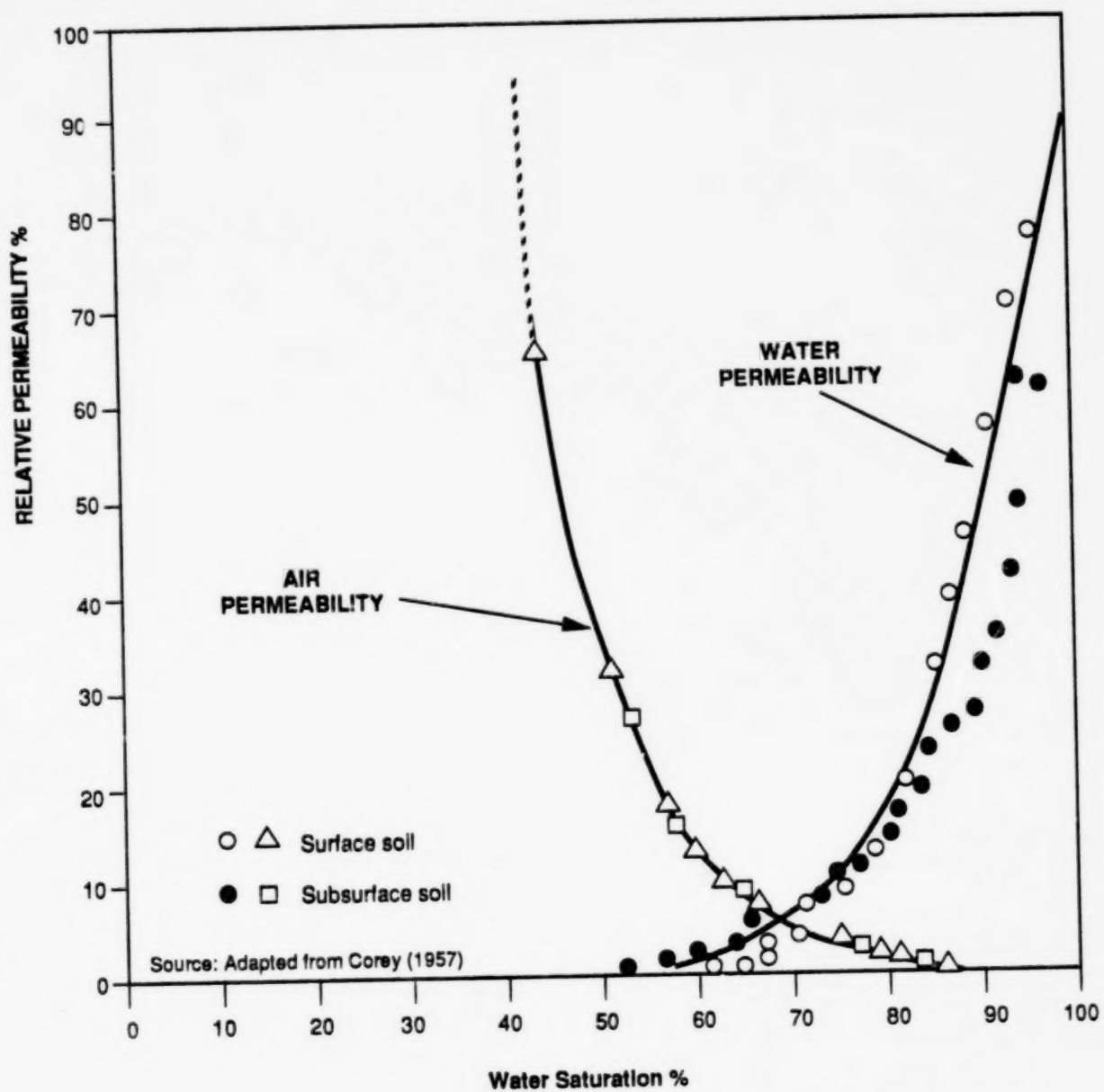


Figure 4. Air and Water Permeability as a Function of Water Content

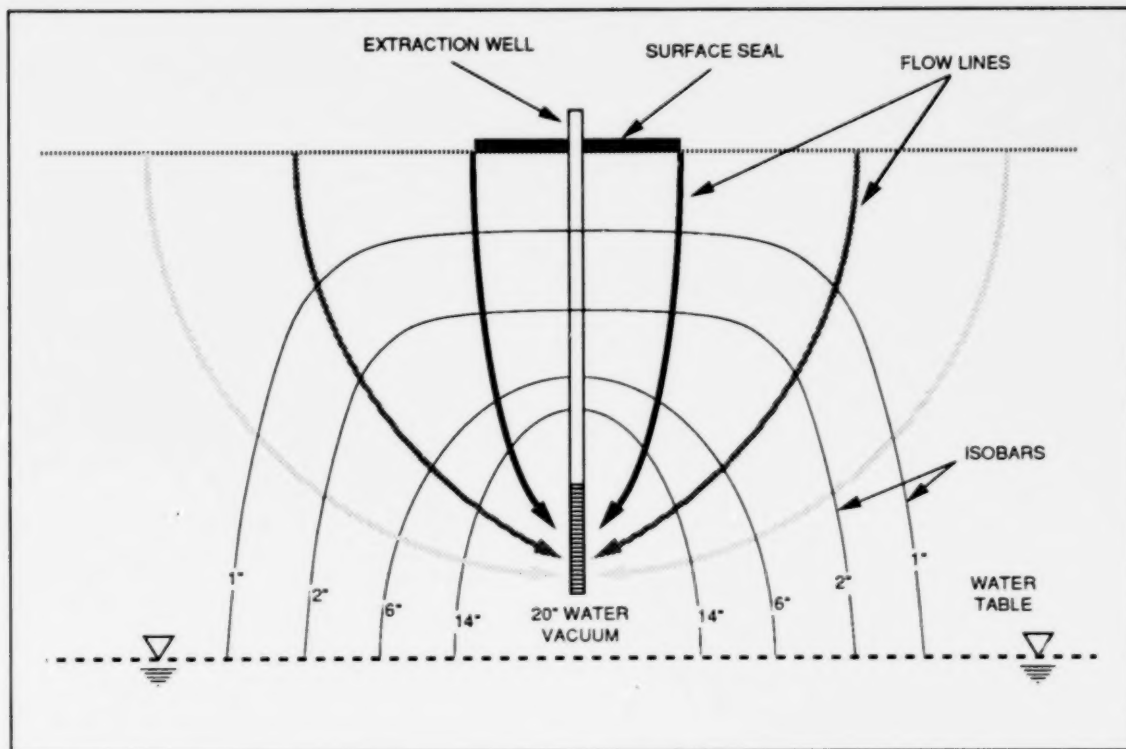


Figure 5. Relationship of Flow and Induced Vacuum

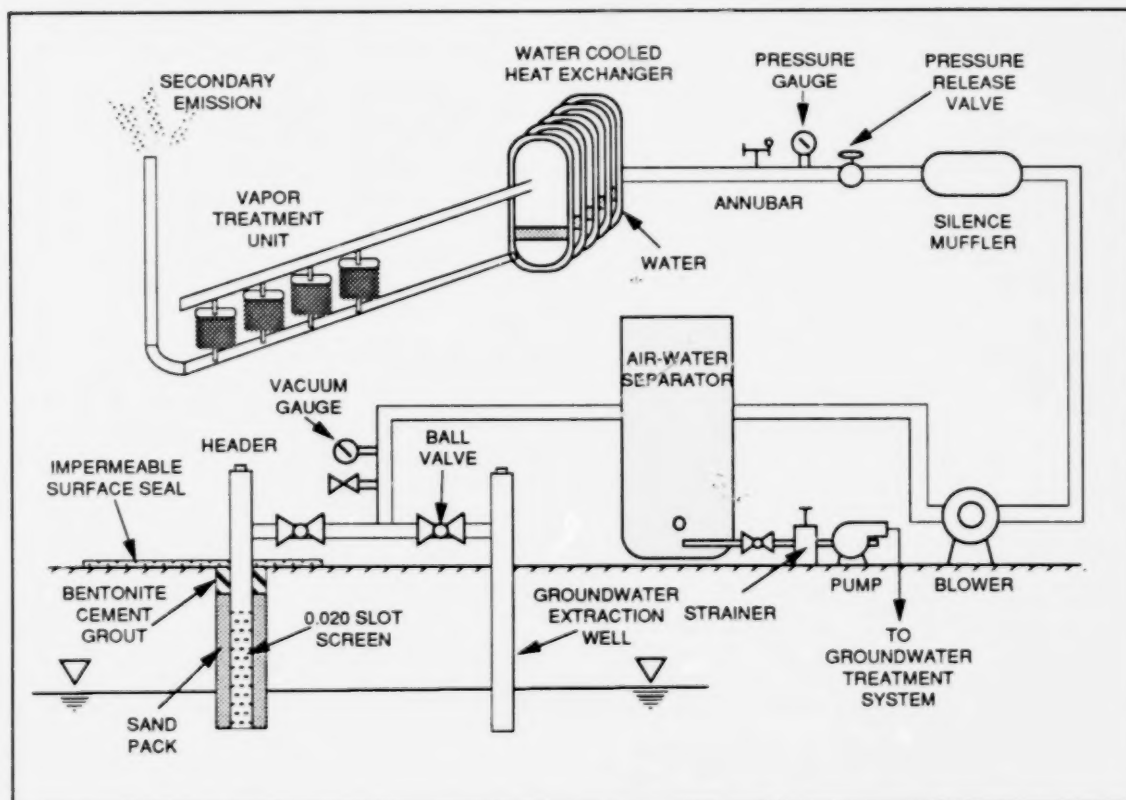


Figure 6. Typical Soil Vapor Extraction System Schematic

ALGASORB®: A NEW TECHNOLOGY FOR REMOVAL AND RECOVERY OF METAL IONS FROM GROUNDWATERS

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ABSTRACT

A new sorption process for removing toxic metal ions from water has been developed. This process is based upon the natural, very strong affinity of biological materials, such as the cell walls of plants and microorganisms, for heavy metal ions. Biological materials, primarily algae, have been immobilized in a polymer to produce a "biological" ion exchange resin, called AlgaSORB®. The material has a remarkable affinity for heavy metal ions and is capable of concentrating these ions by a factor of many thousand-fold. Additionally, the bound metals can be stripped and recovered from the algal material in a manner similar to conventional resins.

This new technology has been demonstrated to be an effective method for removing toxic metals from groundwaters. Metal concentrations can be reduced to low parts per billion (ppb) levels. An important characteristic of the binding material is that high concentrations of common ions such as calcium, magnesium, sodium, potassium, chloride and sulfate do not interfere with the binding of heavy metals. Waters containing a total dissolved solids (TDS) content of several thousand and a hardness of several hundred parts per million (ppm) can be successfully treated to remove and recover heavy metals. The process has been demonstrated under the SITE Emerging Technology program for the effective removal of mercury from a contaminated groundwater.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

In recent years there has been increased attention focused on pollution of water supplies by heavy metal ions. These metals are toxic in rather low concentrations and can lead to acute and chronic illness in humans and other animals. Past waste disposal practices have resulted in serious contamination of the environment. The major sources of heavy metals are leachates from legal and illegal landfills and drainage from old mines. Several of the sites on the National Priorities List are landfill facilities that have problems caused by improper placement of heavy metal wastes below ground.

Chemical treatment using lime or caustic precipitation has been the most common method of removing dissolved metals from leachates, mine drainages, and contaminated aquifers. Other treatments include reverse osmosis, electrodialysis, and carbon adsorption. The energy and chemical costs of these various methods become major operating expenses during the use of these treatments. A serious limitation of many of the current treatment technologies is the difficulty and/or expense of treating waters for removal of heavy metals to allowable drinking water levels. Alternatives for economical recovery of dissolved metals from contaminated waters are limited. The development of rapid, widely applicable, low cost methods for the removal, recovery and recycling of heavy metal ions from contaminated waters at Superfund sites is a high priority.

For a number of years Bio-Recovery Systems has been working with a new sorption process for removing heavy metal ions from water (1-4). This sorption process is based upon the natural, very strong affinity of the cell walls of algae for heavy metal ions. Algal cells have been immobilized in a silica gel polymer (AlgaSORB®) and used much as an ion-exchange resin. The algae are killed in the immobilization process indicating that sorption does not require a living organism, and hence the algal matrix can be exposed, with little or no ill effects, to solution conditions which would normally kill living cells. The pores of the polymer are apparently large enough to allow free diffusion of ions to the algal cells, since similar concentrations of metal ions are bound by free and immobilized cells.

AlgaSORB® functions as a "biological" ion exchange resin and binds both metallic cations and metallic oxoanions. Anions such as chloride or sulfate are only weakly bound or not bound at all. Like ion-exchange resins, the algae-silica system can be recycled. Metal ions have been sorbed and stripped over as many as 75 cycles with no noticeable loss in efficiency. In contrast to current ion exchange technology, however, another real advantage of the algae-silica matrix is that the components of hard water (Ca^{+2} , Mg^{+2}) or monovalent cations (Na^{+} , K^{+}) do not significantly interfere with the binding of toxic, heavy metal ions (2, 3). The binding of Ca^{+2} and Mg^{+2} to ion-exchange resins often limits its usefulness

since these ions are frequently present in high concentrations and compete for heavy metal ion binding. Frequent regeneration of ion-exchange resins is necessary in order to remove heavy metal ions from solution. Another advantage of AlgaSORB® is that it has a high affinity for metal ions. Effluents from AlgaSORB® columns frequently show that metal ions can be reduced to the part per billion level. AlgaSORB® can be used to remove aluminum, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, nickel, platinum, silver, uranium, vanadium, and zinc. Many of these metals are hazardous wastes at Superfund sites.

A major advantage of AlgaSORB® is that the efficiency of heavy metal ion removal is not diminished by the presence of organic compounds in the water. For example, waters containing copper ion and high concentrations of organics such as butyl cellosolve, alcohols, other etchers and halogenated hydrocarbons have been successfully treated (4). Humic and fulvic acids seem to have little or no effect on metal ion binding to AlgaSORB®. The presence of organic compounds limits the usefulness of ion exchange resins since organics often will bind to these resins and decrease their metal binding capacity.

In 1988, Bio-Recovery Systems was selected to participate in the Superfund Innovative Technology Evaluation (SITE) Emerging Technologies Program. The goal of the project was to test AlgaSORB® for the removal of mercury from a contaminated groundwater.

DESCRIPTION OF GROUNDWATERS

A number of years ago an industrial process using mercury resulted in soil contamination with elemental mercury. The mercury subsequently percolated through the soils and contaminated groundwater. At some point the mercury was oxidized to the bivalent oxidation state and was found at various concentrations in the groundwaters depending upon the monitoring site. Currently, the groundwaters are extracted from an upper perched groundwater table via a drainage gallery. A facility has been constructed to treat extracted groundwaters by the use of precipitation with dithiocarbamates, followed by polishing with activated carbon and a specialty ion exchange resin. The water is pumped from the gallery at mercury concentrations of 0.1-3.0 ppm and is currently treated to allowable discharge limits of 10 ppb mercury.

Wells monitoring the ground water during the late 1980's showed seasonal variations in the mercury concentrations. It appears that mercury levels decrease in the dry seasons compared to the rainy seasons. Chemical speciation of the mercury in the groundwaters was not rigorously determined, but speciation studies on soils overlying the groundwater indicated the predominant species was oxidized inorganic mercury. The composition of other elements in the groundwater seems to change with the seasons as well, but an average composition is given in Table 1. Variations in mercury content over a four-year monitoring period in waters from two wells, which are well separated from one another, are shown in Table 2.

TABLE 1. AVERAGE COMPOSITION OF MERCURY-CONTAINING GROUNDWATERS

Constituent	Concentrations (mg/L)
Chloride	5,800
Sodium	2,900
Calcium	460
Magnesium	440
Total Dissolved Solids	11,000
pH	8.0

TABLE 2. SEASONAL VARIATION OF MERCURY CONCENTRATION IN MONITORING WELLS

Month/Yr	Well 1 (mg/L)	Well 2 (mg/L)
Oct/1	9.60	0.370
Nov/1	3.35	0.293
Dec/1	0.29	0.426
Jan/2	5.50	0.230
Mar/2	3.80	0.390
Apr/2	10.00	0.200
May/2	4.20	0.300
Sep/2	7.70	0.370
Dec/2	6.10	0.510
Feb/3	6.20	0.500
Sep/3	8.50	0.240
Dec/3	2.70	0.140
Apr/4	4.00	-
May/4	4.00	0.260
Jun/4	4.40	0.170
Aug/4	5.80	0.180
Sep/4	7.70	0.086
Oct/4	13.00	0.240

EXPERIMENTAL PROCEDURES

Mercury analyses were performed using the EPA Method 245.1 of cold vapor atomic absorption spectroscopy (5). A Perkin Elmer Model 3030B AAS instrument was calibrated daily for mercury, and a calibration verification record was maintained using data collected by the analysis of EPA certified check standards. Preparation of standards for mercury analysis were performed in accordance with

the specifications in Methods for the Chemical Analysis of Water and Wastes (5). Spiked samples were analyzed with each batch of samples to determine if matrix interference existed, and frequent blanks were run to ensure there was no mercury carry over during analysis.

Mercury concentrations in groundwaters, column effluents and regenerating solutions were determined by linear regression calibration curves generated from four point standard calibration analysis. (5).

Samples collected in the field pilot studies were split and sent to Woodward-Clyde Consultants, EER Technologies and Bio-Recovery Systems for mercury analysis.

Laboratory tests on the efficiency of mercury adsorption on AlgaSORB® were determined using small glass columns (1.5 cm i.d. x 20 cm) which contained the sorbent. Mercury-containing groundwaters were pumped through the column at flow rates which varied from 6-20 bed volumes per hour. Effluents from the columns were collected using a fraction collector and mercury content was determined. Once the columns became saturated or leaked mercury above discharge limits (10 ppb), the column was stripped with 10-bed volumes of a selected stripping reagent followed by 10-bed volumes of deionized water. Analyses of stripping effluents were performed to verify stripping.

Pilot studies were conducted with a small portable effluent treatment system which has two AlgaSORB®-containing columns in series and which is capable of treating flows of up to 0.5 gpm. On-site pilot testing was conducted on August 30 to September 1, 1989 and November 6 to December 1, 1989.

RESULTS AND DISCUSSION

Samples of groundwater were collected at various times during 1989. All samples were acidified to pH 2 with nitric acid in the field prior to transport for laboratory studies. Once the samples were received at Bio-Recovery Systems, the solutions were neutralized to the original pH with dilute sodium hydroxide. Laboratory and field studies were complicated by the fact that over a 10 month period, mercury concentrations changed by an order of magnitude. Table 3 shows mercury concentration variation over the sampling period.

Different species of algae can be immobilized to produce different AlgaSORB® resins. Since different biopolymers comprise the cell walls of different algae, some species of algae behave differently from others with respect to metal ion binding. Thus, different AlgaSORBs containing different algal species were tested for mercury removal from the groundwaters. However, these experiments were complicated by the fact that consistent mercury removal performance was not observed using a single immobilized alga on waters collected at different times. For example, Table 4 shows mercury contents in effluents from columns containing AlgaSORB 602. The results shown in Table 4 can not simply be explained by variation in mercury content in the influent waters. For example,

Column C shows lower leakage levels of mercury than column B in the first 40 bed volumes of effluent even though the influent concentration of mercury was nearly three times higher in column C than column B. This suggests that a variation in the chemical species of mercury may occur with time.

TABLE 3. MERCURY CONCENTRATIONS IN GROUNDWATERS

Sample Number	pH	Mercury Concentration ($\mu\text{g/L}$)	Date Collected
103-13089	8.5	150	01-30-89
176-42089	8.0	435	04-20-89
177-42089	8.0	144	04-20-89
265-070589	7.9	1120	07-05-89
343-090189	7.8	620	08-31-89
368-100489	7.9	1550	10-04-89
369-100489	7.9	1550	10-04-89

TABLE 4. TEST OF AlgaSORB 602 ON MERCURY-CONTAMINATED GROUNDWATERS[†]

Bed Volumes of Effluent	A*	B*	C*
	Effluent Hg ($\mu\text{g/L}$)	Effluent Hg ($\mu\text{g/L}$)	Effluent Hg ($\mu\text{g/L}$)
1-4	0.5	9.9	1.3
17-20	0.8	10.1	3.4
37-40	1.3	21.8	8.1
54-60	4.0	14.8	27.0
69-72	-	-	72.5
73-76	2.2	31.0	
93-96	2.3		
113-116	3.0		
133-136	5.0		
149-152	6.5		

[†] Groundwaters collected at various times were pumped at a flow rate of 6 bed-volumes per hour through identical columns containing AlgaSORB 602. Effluents from each column were collected in four bed-volume fractions and analyzed for mercury content. Influent flow rate was six bed volumes per hour.

* Column A influent water was collected January 30, 1989, and had an influent mercury concentration of 150 $\mu\text{g/L}$. Column B influent water was collected April 20, 1989, and had an influent mercury concentration of 435 $\mu\text{g/L}$. Column C influent water was collected July 5, 1989, and had an influent mercury concentration of 1120 $\mu\text{g/L}$.

Over 99 percent of the mercury was stripped from the columns in Table 4 by the passage of 10 bed volumes of 1.0 M sodium thiosulfate through the column (data not shown).

After examining several different AlgaSORB® preparations and noting similar types of variations as shown in Table 4, it was decided to settle on two different AlgaSORB® resins for final testing. While these two resins could have been blended into a single column, they were placed in two columns which were connected in series and from which effluents samples could be taken from each column for mercury analysis. Table 5 shows results of these experiments.

Data in Table 5 show that the two columns arranged in series were effective in mercury removal to below one ppb through passage of 250 bed volumes of mercury contaminated waters which contained 1550 ppb mercury.

On-site pilot testing of the AlgaSORB® resins was performed from November 6, 1989, to December 1, 1989. Two columns (2.54 cm i.d. x 81 cm) were separately filled with AlgaSORB 624 and AlgaSORB 640. The columns each had a bed volume of 400 mL and were connected in series. Mercury-contaminated waters were pumped through the two columns and two bed-volume fractions (800 mL) were collected, split and sent to EER Technologies, Woodward-Clyde and Bio-Recovery Systems for analysis. Results of on-site pilot testing are shown in Table 6.

TABLE 5. TEST OF AlgaSORB 624 AND AlgaSORB 640 ON MERCURY-CONTAMINATED GROUNDWATERS*

Bed Volumes of Effluent	Effluent Hg (µg/L)
0-12	0.3
12-24	0.2
24-36	0.2
48-60	0.3
60-72	0.5
84-96	0.7
108-112	0.8
132-144	0.9
168-180	0.8
192-204	0.9
252-264	0.6
288-300	0.6
312-324	2.0
324-336	1.9

*Two columns (1.0 cm i.d. x 37 cm) coupled in series were used. Groundwaters collected October 4, 1989, and containing 1550 µg/L mercury were passed through the columns at a rate of six bed-volumes per minute. Ten bed volume fractions were collected and analyzed for mercury. Data shown above are mercury concentrations in effluents from the second column.

By the time the on-site testing had begun in November the mercury concentration in the groundwaters had changed from about 1500 ppb (in October) to about 700 ppb (see Table 6). With the exception of the first fraction collected, the data in Table 6 shows that over 500 bed volumes of mercury-contaminated waters were treated before mercury in effluents approached the 10 ppb discharge limit.

TABLE 6. ON-SITE PILOT TESTING FOR MERCURY REMOVAL FROM GROUNDWATERS[†]

Bed Volumes of Effluent	Influent	Mercury Concentration (µg/L)		
		Bio-Recovery Analysis	Woodward Clyde Analysis	EER Technologies Analysis
7-8		9.5	14.2	11
85-86		5.3	8.0	<10
163-64		2.1	3.6	<10
229-230		1.4	1.4	<10
289-290		1.8	2.6	<10
313-314		1.9	2.4	<10
343-344		5.5	9.3	10.0
379-380		2.0	3.1	<10
415-416		1.8	3.2	<10
449-450		4.9	7.8	10.0
467-468		4.0	7.2	<10
503-504		5.8	9.6	<10
533-534		7.7	10.3	<10
587-588		10.5	13.0	15
-----	436*	660	780	620
-----	600*	770	590	720

[†] A portable water treatment system was equipped with two columns connected in series. The first column was filled with AlgaSORB 624 and the second was filled with AlgaSORB 640. Groundwaters were pumped through the system at a flow rate of 6 bed-volumes per hour. Effluent samples were collected and sent to Woodward Clyde Consultants, EPA (EER Technologies Corporation) and Bio-Recovery Systems for analysis.

* Influent samples were collected for analysis just prior to 436 and 600 bed volume fractions of effluent were collected.

CONCLUSIONS

Initial laboratory testing of AlgaSORB[®] resins clearly showed promise for mercury recovery from contaminated groundwaters. Once the mercury was loaded on the resin, it could be stripped with sodium thiosulfate. On-site pilot testing confirmed the laboratory studies and showed that AlgaSORB[®] resins treated over

500 bed volumes of groundwaters before mercury levels in effluents exceeded discharge limits.

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A SITE DEMONSTRATION OF ULTROX UV/OXIDATION TECHNOLOGY

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ABSTRACT

This paper presents the field demonstration test activities and test results of the ultraviolet (UV) radiation/oxidation technology developed by On-Site Ultrox International of Santa Ana, California. The technology simultaneously uses UV radiation, ozone, and hydrogen peroxide to oxidize dissolved organic contaminants present in groundwater or wastewater. The demonstration was performed in February and March of 1989 at the Lorentz Barrel and Drum (LB&D) site in San Jose, California, under the Superfund Innovative Technology Evaluation (SITE) program.

The Ultrox system was evaluated for its effectiveness in treating the volatile organic compounds (VOCs) present in groundwater at the LB&D site. Experiments were conducted in which hydraulic retention time, ozone dose, hydrogen peroxide dose, UV radiation intensity, and influent pH level were varied over a wide range to assess the system's performance.

The Ultrox system achieved VOC removals of greater than 90 percent. Most VOCs were removed through chemical oxidation. However, for a few VOCs such as 1,1,1-trichloroethane and 1,1-dichloroethane, stripping also contributed toward removal. The treated groundwater met the applicable discharge standards at 95 percent confidence level for discharge into a local waterway. There were no harmful air emissions to the atmosphere from the Ultrox system, which is equipped with an off-gas treatment unit.

This paper has been reviewed in accordance with U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Technologies to destroy, treat, detoxify, reduce mobility, or volume, or recycle hazardous waste materials are being developed and demonstrated within the Environmental Protection Agency (EPA). The Superfund Innovative Technology Evaluation (SITE) Program was created in 1986 to provide information on alternative and innovative technologies. The SITE program also generates reliable performance and cost data for these technologies from each demonstration, as well as a broader range of data on each process from non-SITE activities.

The On-Site Ultrox International's proposal for ultraviolet radiation (UV)/oxidation technology was selected in 1988 for the SITE program, by the EPA's Office of Research and Development (ORD) and Office of Solid Waste and Emergency Response (OSWER). Upon approval of EPA's Region IX and agreement between On-Site Ultrox International, ORD, and OSWER, the technology was demonstrated at the Lorentz Barrel and Drum (LB&D) site in San Jose, California.

LORENTZ BARREL AND DRUM SITE HISTORY

The LB&D site located in San Jose, Santa Clara County, California, was used primarily for drum recycling operations from about 1947 to 1987. The drums contained residual aqueous wastes, organic solvents, acids, metal oxides, and oils. The preliminary site assessment report for the LB&D site showed that the ground water and soil were contaminated with organics and metals (1).

The upper aquifer at the LB&D site was selected as the waste stream for evaluating the UV/oxidation technology. Samples from the shallow aquifer were collected in December 1988 which indicated volatile organic compounds (VOCs) were present. VOCs detected at high levels included trichloroethylene (280 to 920 $\mu\text{g/L}$), vinyl chloride (51 to 146 $\mu\text{g/L}$), and 1,2-trans-dichloroethylene (42 to 68 $\mu\text{g/L}$). The pH and alkalinity of the ground water were about 7.2 and 600 mg/L as CaCO_3 , respectively. These measurements indicated that the bicarbonate ion (HCO_3^-), which acts as an oxidant scavenger, was present at high levels. Other oxidant scavengers, such as bromide, cyanide, and sulfide were not detected.

UV/OXIDATION EQUIPMENT AND PROCESS DESCRIPTION

Major components of the Ultrox system include the UV/oxidation reactor module, an air compressor/ozone generator module, a hydrogen peroxide feed system, and a catalytic ozone decomposition (Decompozon) unit. The Ultrox treatment system uses UV radiation, ozone, and hydrogen peroxide to oxidize organics in water. An isometric view of the Ultrox system is shown in Figure 1.

During the operation, contaminated water first comes in contact with hydrogen peroxide as it flows through the influent line to the reactor. An in-line static mixer is used to disperse the hydrogen peroxide into the contaminated water. Next, the water comes in contact with UV radiation and ozone as it flows through the reactor at a specified rate to achieve the desired hydraulic retention time. As the ozone gas in the reactor is transferred to the contaminated water, hydroxyl radicals ($\text{OH}^\bullet$) are produced. The hydroxyl radical formation from ozone is catalyzed by UV radiation and hydrogen peroxide. Hydroxyl radicals are known to react with organics more rapidly than the oxidants, ozone, hydrogen peroxide, and UV radiation. Ozone that is not transferred to the contaminated water will be present in the reactor off-gas, which will be ultimately destroyed by the Decompozon unit before being vented to the atmosphere.

The demonstration reactor (Model PM-150) has a volume of 150 gallons and is 3 feet long by 1.5 feet wide by 5.5 feet high. The reactor is divided by 5 vertical baffles into 6 chambers and contains 24 lamps (65 watts each) in quartz sheaths. The UV lamps are installed vertically and are evenly distributed throughout the reactor (four lamps per chamber). Each chamber has one stainless steel sparger that extends along the width of the reactor. These spargers uniformly diffuse ozone gas, supplied from the ozone generator module, from the base of the reactor into the water.

The Decompozon unit (Model 3014 FF) uses a nickel-based proprietary catalyst to convert reactor off-gas ozone to oxygen. The Decompozon unit can accommodate flows of up to 10 standard cubic feet per minute and can destroy ozone concentrations in ranges of 1 to 20,000 ppm (by weight) to less than 0.1 ppm.

TECHNOLOGY DEMONSTRATION

The demonstration was designed to meet the following objectives: (1) evaluate the performance of the Ultrox system in treating the VOCs present in the ground water at the LB&D site under different operating conditions; (2) determine the extent of VOC stripping; (3) evaluate the efficiency of the Decompozon unit to destroy reactor off-gas ozone; and (4) determine the operating conditions needed for the effluent to meet applicable discharge standards (NPDES).

TESTING APPROACH

The test operation was designed for 11 test runs. After these runs, two additional runs were performed to determine if the system's performance was reproducible. These operating conditions are summarized in Table 1. All 13 runs were performed over a period of two weeks.

Five operating parameters including (1) influent pH, (2) retention time, (3) ozone dose, (4) hydrogen peroxide dose, and (5) UV radiation intensity were adjusted within specified ranges. The initial operating

conditions (Run 1), were based on the results of a treatability study performed by Ultrox on the LB&D site ground water for Region IX.

Three indicator VOCs were selected for preliminary testing after each run. These were trichloroethylene (TCE, a major volatile contaminant at the site), 1,1-dichloroethane (1,1-DCA), and 1,1,1-trichloroethane (1,1,1-TCA). The latter two were selected because these VOCs are relatively difficult to oxidize. These indicator VOCs were analyzed overnight. Once the preferred level (operating conditions at which the effluent concentrations of indicator VOCs were below NPDES limits, and the relative operating costs were the lowest) was determined from the overnight analysis, that parameter remained at that level for the remaining runs. The pH was adjusted by adding sulfuric acid in the first three runs. After the preferred values were determined for all five operating parameters, two runs (12 and 13) were performed to verify the reproducibility of the Ultrox system's performance.

SAMPLING AND ANALYTICAL PROCEDURES

Air and liquid samples were collected from the Ultrox system at nine locations. The liquid samples were collected from: (1) hydrogen peroxide feed tank; (2) acid feed tank (when the pH was adjusted); (3) raw influent line; (4) influent line after acid and hydrogen peroxide addition (when pH was adjusted); (5) mid-point of the reactor; and (6) effluent line. The air samples were collected from: (1) ozone gas feed line; (2) reactor off-gas line; and (3) treated off-gas.

For the critical parameters in this study (VOCs in water), six replicate samples were collected. Duplicate samples were collected for several noncritical parameters. Sampling at the influent port began about 15 minutes after each run was started. At other locations in the reactor, sampling began after three retention times to allow the system to reach steady state. All samples for off-site laboratory analysis were preserved as required before being shipped to the laboratory. Details on the quality assurance and quality control procedures are presented in the Demonstration Plan and the Technology Evaluation Report (2,3).

RESULTS

Results of the Ultrox system are summarized to present the overall effectiveness of the UV/oxidation technology in removing VOCs from the ground water at the LB&D site. The removal efficiencies and concentration profiles of all VOCs are not presented in this paper.

REMOVAL OF VOCs

Based on overnight analysis performed during the demonstration (when two of the six replicates determined the average effluent concentrations for each indicator VOC), Runs 8 and 9 showed that the effluent met the discharge standard at either set of conditions. Since a lower hydrogen peroxide dose

was used in Run 9, compared to Run 8, Run 9 was chosen as the preferred operating run. However, based on a complete analysis of the four remaining replicates for Run 9 performed after the demonstration, the mean concentration of 1,1-DCA was found to be slightly higher than 5 $\mu\text{g/L}$, the discharge standard for the VOC. Since Run 9 had the preferred operating conditions during the demonstration, the verification runs (12 and 13) were also performed at those conditions.

A comparison at 95 percent upper confidence limits was made for the effluent VOCs in Runs 9, 12, and 13. These limits were calculated using the one-tailed Student's t-test. The effluent met the discharge standards for all regulated VOCs at 95 percent confidence level in Runs 12 and 13. In Run 9, the mean concentrations for 1,1-DCA and 1,2-DCA exceeded the discharge standards.

Percent removals for the indicator VOCs and total VOCs decreased considerably in Run 7 (Figure 2). This appears to be due to the decreased ozone dose applied in Run 7. Removal efficiencies for TCE were higher than those for 1,1-DCA and 1,1,1-TCA. This finding is consistent with the rationale used in selecting the indicator VOCs.

To determine the extent of VOC removal attributed to stripping within the treatment system, VOC samples were collected from the reactor off-gas. A total of 25 samples were collected during the demonstration. Four VOCs frequently detected were TCE, vinyl chloride, 1,1,1-TCA and 1,1-DCA. Reactor off-gas VOC emission rates were compared to the VOC removal rates (estimated by difference between the VOC input rates at the influent and output rates at the effluent ports of the Ultrox system). Results are summarized in Table 2. The extent of stripping for any particular VOC is expected to be proportional to the ratio of air flow rate to the water flow rate. The ratio for Runs 1 to 5 is approximately 2; for Run 6 and Runs 8 to 13, it is about 4.5; and for run 7, it is 1. If stripping contributed to the total removal of the four VOCs, the extent of stripping should be the least in Run 7, and the most in Runs 6 and 8 to 13. The data presented in the table follow this trend for three of the four VOCs (except for the vinyl chloride in Runs 6, 7, and 9). A quantitative correlation of the extent of stripping cannot be made because the operating conditions in each run were different. For example, at a given air to water flow ratio, when oxidation doses are varied, the extent of oxidation also varies. Therefore, the extent of stripping will be indirectly affected.

Henry's law constants for the four VOCs are also presented in Table 2. When comparing these constants with the VOCs, their volatility is expected to increase from left to right:

1,1-DCA ---> TCE ---> 1,1,1-TCA ---> vinyl chloride

However, significant removals for 1,1,1-TCA and 1,1-DCA were observed to be due to stripping. Conversely, the extent of stripping was low for

vinyl chloride and TCE which possess double bonds between the carbon atoms. Based on these results, stripping is a significant removal pathway for compounds that are difficult to oxidize.

DECOMPOZON UNIT

Ozone concentrations in the influent to and the effluent from the Decompozon unit were analyzed in each run. The effluent ozone concentrations were low (less than 0.1 ppm) for Runs 1 to 8, approximately 1 ppm in Runs 9 and 10, and greater than 10 ppm in Runs 11, 12, and 13. A malfunctioning heater in the Decompozon unit from runs 11 to 13 created high ozone levels (greater than 1 ppm). The temperature in the Decompozon unit should have been 140°F for the unit to function properly, whereas the temperature for Runs 11 to 13 was only about 80°F. Ozone destruction efficiencies were achieved greater than 99.99 percent in Runs 1 to 10. Significant VOC removal occurred when the unit functioned as designed (Runs 1 through 8).

NON-CRITICAL PARAMETERS

Non-critical parameters measured included semi-volatile organics, PCBs/pesticides, and total organic carbon (TOC). Non-critical parameters for inorganics included pH, conductivity, and alkalinity. Temperature, turbidity, residual oxidants, and electricity consumption were also measured.

No semivolatiles or PCBs/pesticides were detected in either the influent or effluent. Minimal TOC removal occurred indicating that complete oxidation of organics to carbon dioxide and water did not occur.

Iron and manganese were present at low concentrations, and no significant metal removal occurred. No changes in alkalinity and conductivity were observed after the treatment. However, the pH increased by 0.5 to 0.8 units after the treatment. The increase in pH is attributed to the reaction between hydroxyl radicals and bicarbonate ions (the predominant form of alkalinity at the ground water pH, which is 7.2) in which hydroxyl ions are produced (4).

Turbidity increased by 1 to 4 units after the treatment, which may be due to the insignificant amount of metal removal by oxidation and precipitation. The temperature increased by approximately 5°F after the treatment and was due mainly to the heat from the UV lamps. Ozone gas transfer to the ground water was over 95 percent, with 5 percent remaining in the reactor off-gas before treatment. After the reaction, the residual ozone and hydrogen peroxide concentrations in the effluent were usually less than 0.1 ppm. Electrical consumption averaged about 11 kWh/h of operation.

CONCLUSIONS

The treated ground water met the discharge standards for disposal into a nearby waterway at the 95 percent confidence level at a hydraulic retention time of 40 minutes, an influent pH of 7.2 (unadjusted), an ozone dose of 110 mg/L, a hydrogen peroxide dose of 13 mg/L, and with all 24 UV lamps operating.

The Decompozon unit destroyed the reactor off-gas ozone to levels less than 0.1 ppm (OSHA Standard) with destruction efficiencies greater than 99.99 percent.

Removal efficiencies for TCE and total VOCs were as high as 99 percent and 90 percent, respectively. However, maximum removal efficiencies for 1,1-DCA and 1,1,1-TCA were about 65 percent and 85 percent, respectively.

Both chemical oxidation and stripping occurred in the removal of 1,1-DCA and 1,1,1-TCA. In general, about 12 to 75 percent of the total removals for 1,1,1-TCA, and 5 to 44 percent of the total removals for 1,1-DCA were due to stripping. In most of the runs, stripping for TCE and vinyl chloride was less than 10 percent. For other VOCs, such as 1,1-dichloroethene, benzene, acetone, and 1,1,2,2-tetrachloroethane, stripping was negligible. VOCs present in the gas phase within the reactor at levels of approximately 0.1 to 0.5 ppm were removed to below detection levels in the Decompozon unit.

Very low TOC removal occurred, which implies that partial oxidation of organics took place in the system, but not complete conversion to carbon dioxide and water. However, in the GC and GC/MS analyses performed for VOCs, semivolatile organics, and PCBs/pesticides, no new compounds were discovered.

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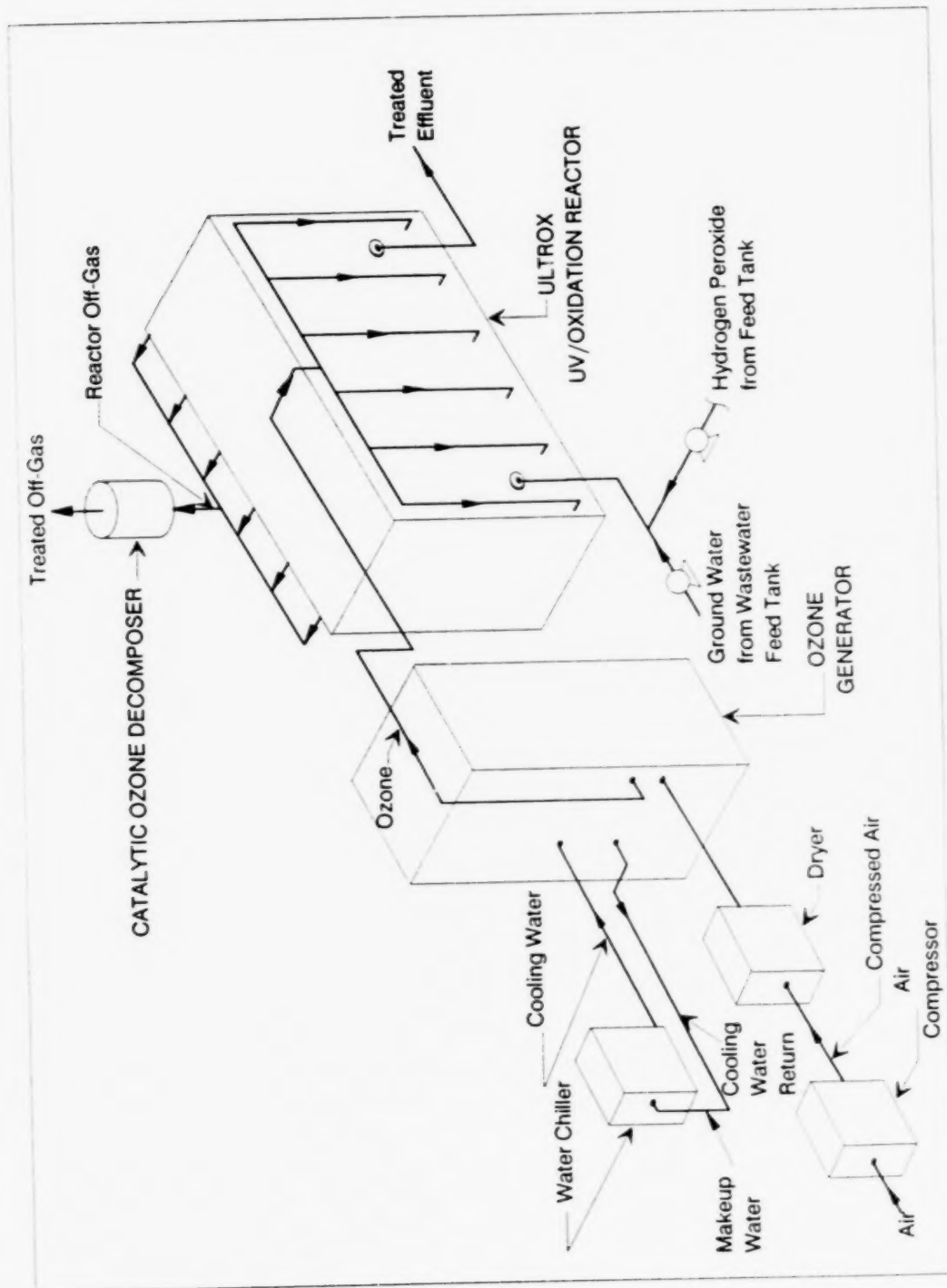


Figure 1. Isometric View of Ultrox System.

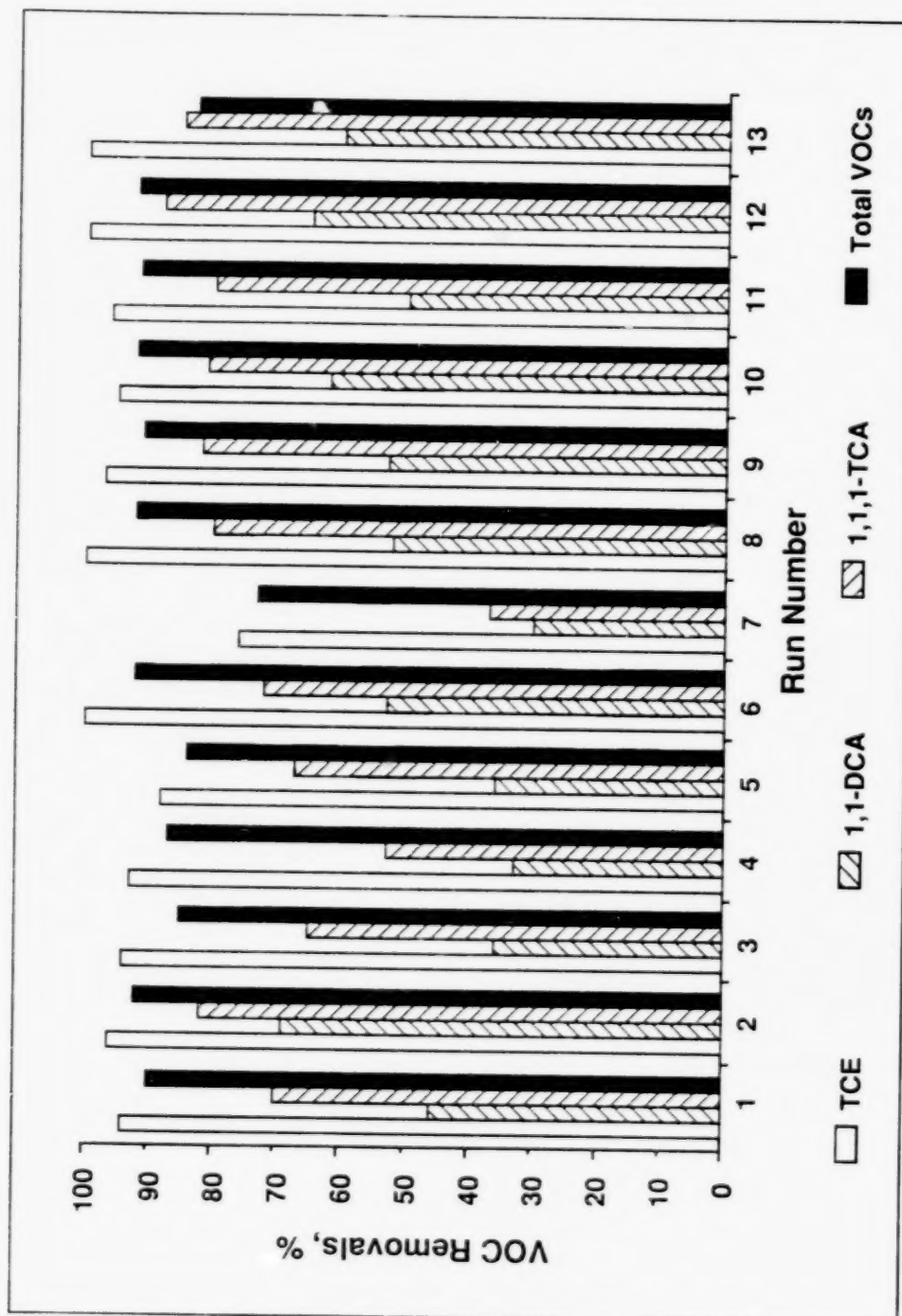


Figure 2. VOC Removals in Different Runs.

TABLE 1. OPERATING PARAMETERS MATRIX

Run No.	Influent pH	Retention Time (min)	Ozone Dose (mg/L of Water)	H ₂ O ₂ Dose (mg/L)	UV Lamps (24 @ 65 W each)
1	7.2	40	75	25	All On
2	6.2	40	75	25	All On
3	5.2	40	75	25	All On
4	7.2	60	75	25	All On
5	7.2	20	75	25	All On
6	7.2	40	110	25	All On
7	7.2	40	38	25	All On
8	7.2	40	110	38	All On
9	7.2	40	110	13	All On
10	7.2	40	110	13	1-12 On
11	7.2	40	110	13	13-24 On
12	7.2	40	110	13	All On
13	7.2	40	110	13	All On

TABLE 2. EXTENT OF VOC STRIPPING IN THE ULTROX SYSTEM

Run No.	$\left[\frac{\text{Air Flow Rate}}{\text{Water Flow Rate}} \right]$	Percent Stripping Contribution for			
		1,1-DCA	TCE	1,1,1-TCA	Vinyl Chloride
		0.0043†	0.0091†	0.014†	0.082†
1	2.1	7.4	2.0	43	0.013
2	2.3	9.1	3.4	34	0.95
3	2.1	9.9	2.7	31	0.013
4	2.0	7.4	3.0	29	0.010
5	2.1	17	3.5	29	1.7
6	4.5	16	1.2	65	0.072
7	1.0	4.9	1.2	12	3.1
8	4.5	23	7.5	85	1.2
9	4.5	16	6.6	58	0.040
10	4.3	27	9.4	73	1.1
11	4.6	44	24	>99	13
12	4.4	34	7.0	76	8.9
13	4.3	37	26	75	1.8

† Henry's law constant of the VOC, atm-m³/mol.

SITE DEMONSTRATION OF BIOLOGICAL
TREATMENT OF GROUNDWATER BY BIOTROL, INC.
AT A WOOD PRESERVING SITE IN NEW BRIGHTON, MN

by

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ABSTRACT

A wood preserving site in New Brighton, MN on EPA's National Priorities List was selected for evaluation of a groundwater treatment for pentachlorophenol with a fixed-film biological system. The system employs indigenous microorganisms but is also amended with a specific pentachlorophenol-degrading bacterium. The mobile, pilot-scale unit used for the demonstration houses a 540-gallon, three-stage bioreactor filled with structured PVC packing for biomass support. After an initial acclimation period, groundwater from a well on the site was fed to the system at 1, 3, and 5 gpm with no pretreatment other than pH adjustment, nutrient addition, and temperature control. Each flow regime was maintained for about two weeks while samples were collected for extensive analyses.

At 5 gpm, the system was capable of achieving about 96% removal of the pentachlorophenol in the incoming groundwater and producing effluent pentachlorophenol concentrations of about 1 ppm, which met the local POTW requirement for discharge. At the lower flows (1 and 3 gpm) removal was higher (about 99%) and effluent pentachlorophenol concentrations were well below 0.5 ppm.

Operating costs, including power (pumping of liquids and heating), nutrients and caustic, and operator labor, are reported. This system appears to be a compact and cost-effective treatment for pentachlorophenol-contaminated wastewaters. Pre- and post-treatment such as for oil or solids removal, may be required on a site- and wastewater-specific basis.

The results reported in this paper are preliminary and a full report is in preparation. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Soil and groundwater contamination by chemicals commonly resulting from wood preserving operations has frequently been found at Superfund sites on the National Priorities List. Under the Superfund Amendments and Reauthorization Act of 1986 (SARA), the U.S. Environmental Protection Agency was empowered to initiate a Superfund Innovative Technology Evaluation (SITE) program to develop, demonstrate, and evaluate new and innovative technologies that could be used at Superfund sites. A method for the destruction or removal of hazardous chemical species such as pentachlorophenol (PCP) and creosote-derived polynuclear aromatic hydrocarbons (PAHs) found at wood preserving sites was deemed to be suitable for investigation under this program.

BioTrol, Inc. of Chaska, MN offered a biochemical destruction technology and encouraging claims from earlier, small-scale studies that indicated that efficient removal of such pollutants from contaminated soil and groundwater could be achieved. While biotreatment has a long history as a cost-effective destructive method for organic chemicals in both industrial and municipal wastewaters, it was uncertain whether such technology would be effective at Superfund sites for the recalcitrant chemicals that might be encountered as a result of long term wood preserving operations, specifically pentachlorophenol and polynuclear aromatic hydrocarbons.

Subsequently, the BioTrol, Inc. Aqueous Treatment System (ATS) was selected for investigation under the SITE program. After considering alternate sites, a facility recently added to the National Priorities List was chosen for a pilot-scale evaluation of the technology. The selected site, in New Brighton, MN, a suburb of Minneapolis, has been used for wood treatment with various preservatives, including creosote, pentachlorophenol, and chromated copper arsenate since the 1920s. Tests at the site as part of a RI/FS indicated that both the soil and the underlying groundwater were contaminated with pentachlorophenol and polynuclear aromatic hydrocarbons, even though these chemicals were no longer being used in wood treatment. The owner and operator of the site, the MacGillis and Gibbs Company, agreed to host the pilot-scale testing of the BioTrol system.

PROCESS DESCRIPTION

The BioTrol Aqueous Treatment System (ATS) shown in Figure 1 consists of a conditioning or temper tank, a heater and heat exchanger, and a three-stage fixed-film biological reactor. Incoming wastewater is first brought to the conditioning tank where the pH is adjusted (if necessary) to just above 7.0 with caustic and inorganic nitrogen and phosphorus nutrients are added. After passing through the in-line heater and heat exchanger to assure a more constant temperature in the vicinity of 70 F, the wastewater is introduced to the base of the first of the three bioreaction chambers (Figure 2). Each chamber is filled with an inert support for bacterial growth; in the study corrugated polyvinyl chloride sheets were the support medium used (Figure 3). The influent is passed up through each chamber while air is injected at the base of each chamber through a sparger tube system, as shown in Figure 2.

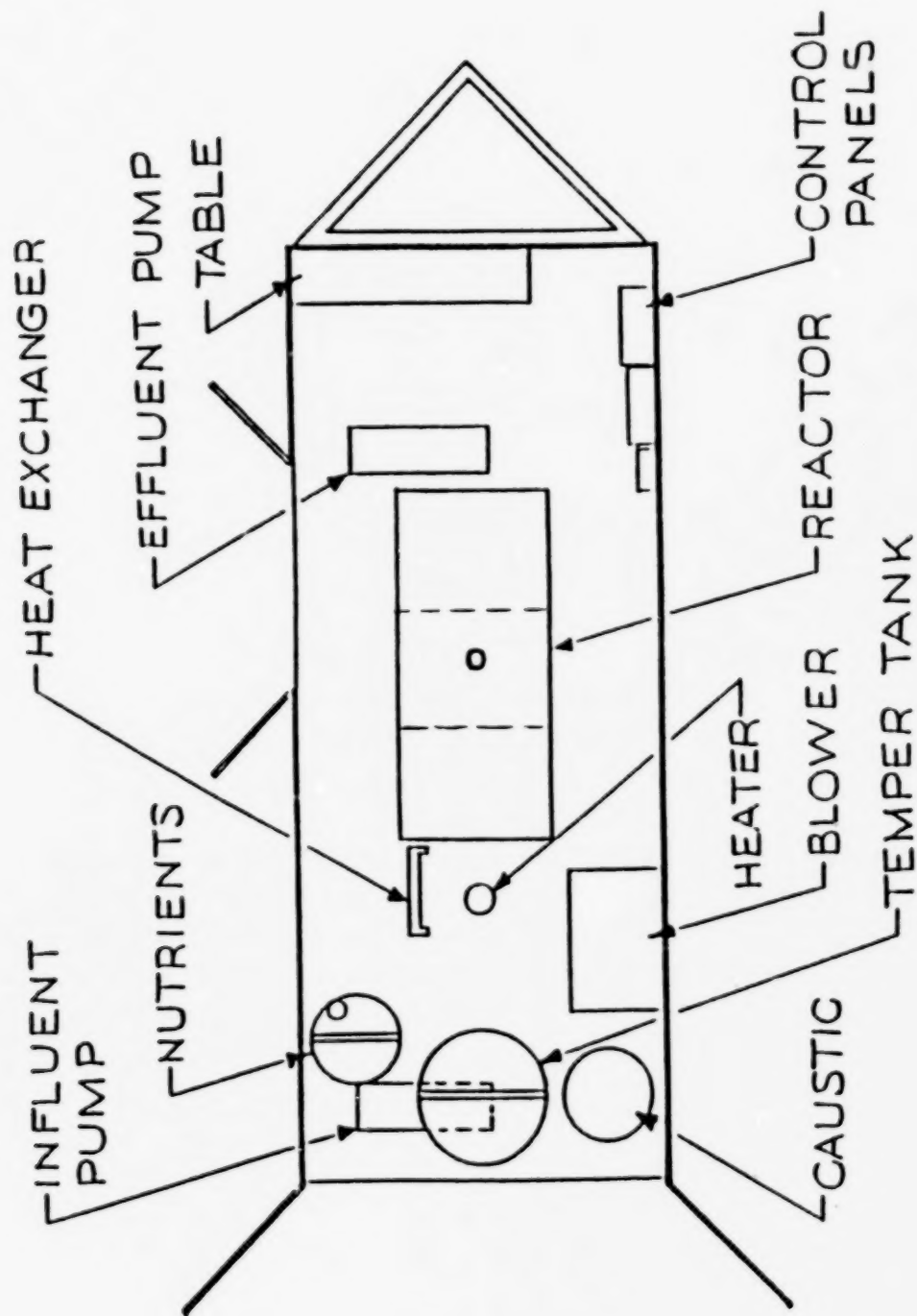
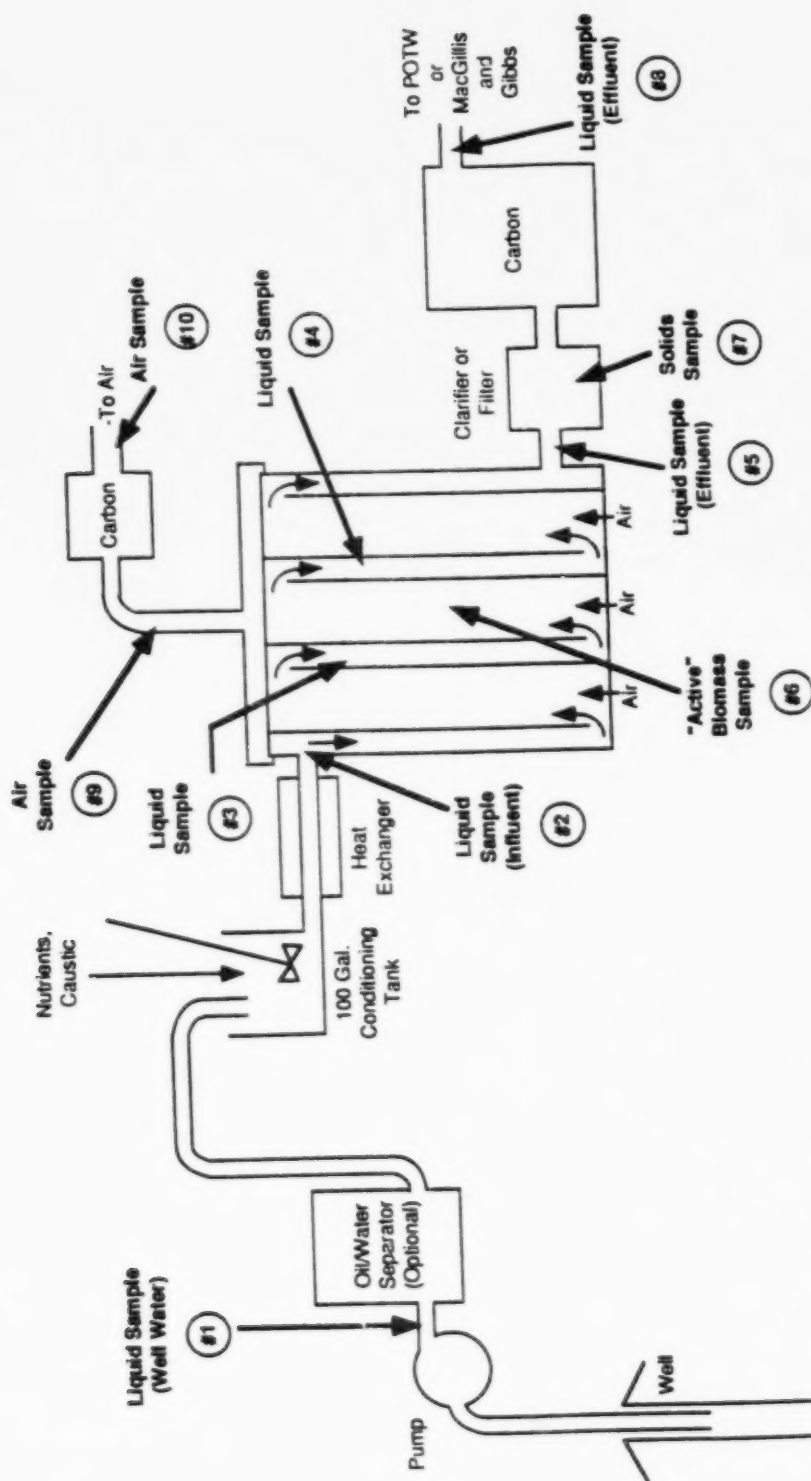


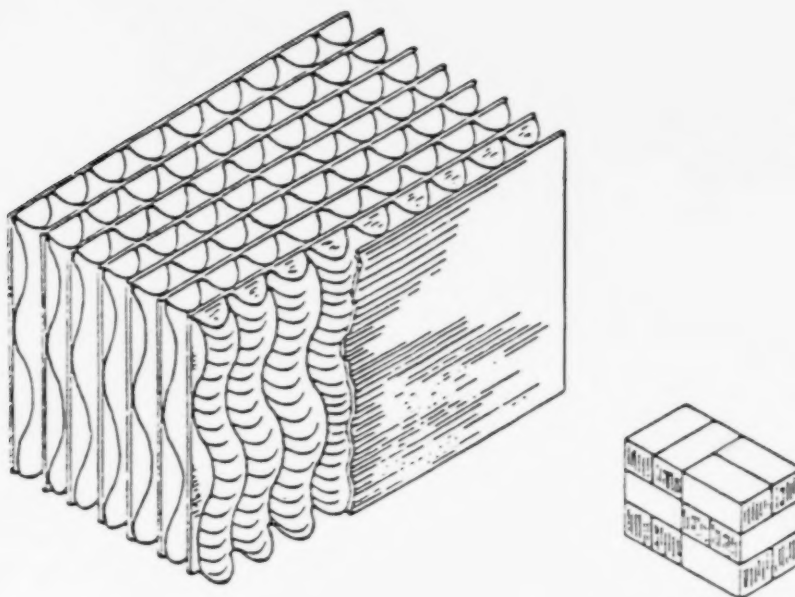
Figure 1. BioTrol, Inc. Mobile Aqueous Treatment System (ATS) System.



Note: Circled numbers at sample points refer to labelling system

Figure 2. Aqueous Treatment System (ATS) with Sampling Points Shown.

FIGURE 3
CORRUGATED POLYVINYL CHLORIDE MEDIA



The system is acclimated by introducing an indigenous bacterial population taken from the local soil. After allowing about one week for acclimation of this growth to the wastewater, the system is "seeded" with an inoculum of a flavobacterium specific to the target contaminant, in this case pentachlorophenol. The wastewater containing the contaminant is then recycled through the system to allow the bacterial population to readjust. When the system is fully adapted to the wastewater, once-through processing is ready to begin.

At the MacGillis and Gibbs site it was determined that the quality of the groundwater did not warrant any pretreatment, even though it contained a significant level of oil (about 50-60 ppm). While pretreatment such as oil/water separation or solids removal may be needed in other cases, such decisions must be site and wastewater specific. Similarly, post-treatment decisions also depend on the specific site. At this facility, a decision was made to install a bag filter to collect the small amount of sloughed biomass that was anticipated, primarily so that pollutants in the sludge could be measured as part of the EPA investigation.

SITE TESTING PROGRAM

Working in collaboration with the developer of the process, it was determined that operation of the system at three increasing flow rates, 1, 3,

and 5 gpm, corresponding to residence times of 9, 3 and 1.8 hours, respectively, each for two weeks, would allow the effectiveness of the process to be determined at low contaminant loadings and at the design level. In fact, while the screening data reported in 1984 as part of the RI/FS had suggested high concentrations (~100-200 ppm) of pentachlorophenol might be present in the groundwater, when two wells were drilled in preparation for the project, a maximum of about 45 ppm pentachlorophenol and only low levels of polynuclear aromatic hydrocarbons (<1 ppm total PAHs) were found to be present.

The groundwater obtained from the selected well, the influent to, the effluent from, and the two intermediate stages of the bioreactor were monitored for pentachlorophenol, other semivolatile organics, chloride, and TOC. Chloride and TOC were monitored to provide supporting evidence for the vendor's claim that pentachlorophenol removal occurred by mineralization to water, carbon dioxide and salt by the following equation.



Other parameters also monitored to provide a complete history of the groundwater as it passed through the system included total and volatile suspended solids, oil and grease, nitrogen and phosphorus, volatile organics, and heavy metals. Because there is always concern when treating wastewaters containing chlorinated aromatics, testing was also done for chlorodioxins and furans.

Because this investigation was part of the SITE program and careful and complete analytical history (and safety) was desirable, carbon adsorption units were installed on both the aqueous discharge and on the air leaving the covered reactor chamber. Samplings and analyses were carried out before and after these units to determine whether significant quantities of the contaminants were lost by any route other than biodegradation.

Finally, static bioassays were carried out on the incoming groundwater, the influent to the reactor, and the effluent to learn whether the groundwater was toxic to aquatic species and whether treatment removed the chemical source of any toxicity.

RESULTS

From comparison of the pentachlorophenol concentrations for the groundwater as removed from the well and the effluent from the bioreactor, it is clear that the BioTrol system is capable of achieving about 96% removal of pentachlorophenol at the design flow rate, 5 gpm. And, at that flowrate, final effluent concentrations, before carbon polishing, are approximately 1 ppm. Table 1 summarizes the pentachlorophenol removals at the three different flow rates.

TABLE 1. AVERAGE PENTACHLOROPHENOL REMOVAL BY
THE BIOTROL AQUEOUS TREATMENT SYSTEM

Flow Rate (gpm)	Ground- water (ppm)	Effluent (ppm)	Percent Removal (%)	
			Average	Range
1	42.0*	0.13	99.8 **	87.4-99.9+
3	34.5*	0.36	98.7 **	95.8-99.8
5	27.5*	0.99	97.6 **	79.3-99.4

* decrease with time may reflect drawdown of aquifer

** based on average of daily effluents

However, it must be noted that as the analytical results were obtained, it became apparent that an unexpected dilution phenomenon was occurring in the influent chamber where the composite influent samples were taken. The effect was a significant reduction in the apparent "influent" concentrations for pentachlorophenol (and other parameters) - and, presumably, in the values at the two intermediate sampling points as well. Where these values should have been essentially the same as the values for the groundwater, it was observed that they were considerably lower. Grab samples obtained by the vendor between the conditioning tank and the bioreactor and analyzed for pentachlorophenol using another method also confirmed the discrepancy. (In this alternate method, high pressure liquid chromatography [HPLC], the aqueous sample is injected directly onto a column at ambient temperature and the levels of pentachlorophenol measured with a UV detector at 254 nm and 220 nm. Although the method is not "EPA-approved" and was not subjected to the extensive quality assurance used for the GC/MS method, an abbreviated evaluation has demonstrated that the results are reliable and comparable to those obtained by GC/MS.) It is believed that the differences in concentrations, which were particularly significant at the lower flow rates, are the result of backmixing from each of the reaction chambers into the preceding mixing chambers. Consequently, the results being presented are based primarily on the incoming groundwater as it was analyzed at the well head and the final effluent from the bioreactor, using EPA Method 3510/8270, for which the Method Detection Limit for pentachlorophenol is 50 ug/L.

At the lower flow rates studied, 1 and 3 gpm, pentachlorophenol removals (based on the change from the groundwater to the effluent) increase to 99+ and final pentachlorophenol concentrations of 0.1 ppm and even less are achievable. These results are summarized in Table 1.

The changes in chloride and TOC results (weekly) parallel the decrease in pentachlorophenol at all flows (Table 2); however, they are not sufficiently precise to provide more than supportive evidence for mineralization of pentachlorophenol to sodium chloride, water, and carbon dioxide.

TABLE 2. COMPARISON OF AVERAGE CHLORIDE, TOC, AND PCP RESULTS

Flow Rate (gpm)	[-----Change (delta)-----]				
	PCP	Cl(f)	Cl(c)	TOC(f)	TOC(c)
		(ppm)			
1	-41.9	+44.2	+27.9	-24	-11.3
3	-34.1	+40.5	+22.7	-32	- 9.2
5	-26.5	+22.0	+17.6	-21	- 7.0

(f) - found; (c) calculated

As part of the effort to confirm that pentachlorophenol was being removed by biochemical mineralization and not by adsorption on the biosolids or by stripping due to the air in the bioreactors, both solids and air emissions were also monitored. Although the sludge trapped in the bag filter was found to contain pentachlorophenol (34 and 170 ppm found in two samples), the amount of sludge was so small that adsorption of pentachlorophenol on the biosolids and removal with the suspended solids does not represent a significant alternate removal mechanism. Thus, even if all the suspended solids (effluent - groundwater) produced by the system during the twelve days of the 1 gpm run were trapped in the filter, this would amount to only about 7 lbs of sludge. Even with a pentachlorophenol content as high as 170 ppm (which was measured in a later sample), this would only account for about 0.0012 lbs of PCP or about 0.02% of the total pentachlorophenol input of about 6.05 lbs. Similarly, pentachlorophenol was not present above the detection limit in any of the air samples obtained over the reactor chamber, using a modified Method 5 collection system with an XAD resin trap and an analytical method with a detection limit of 1.7 ug/cubic meter or 0.2 ppb. Therefore, it does appear that biological degradation is, by far, the primary means of eliminating the pentachlorophenol from the groundwater.

Concentrations of the various polynuclear aromatic hydrocarbons as part of the semivolatile fraction were below detection limits in the samples of incoming groundwater used in the demonstration program. Two analyses during the pre-demonstration testing indicated total PAHs of 145 and 295 ppb; Consequently, it is not possible to draw any conclusions as to removal efficiency or mechanism. However, several PAHs, including naphthalene and methyl naphthalene at maximum levels of 34.6 ppb and 47.9 ppb, respectively, and others at considerably lower levels, were found during the modified Method 5 testing of the air emissions from the reactor. This suggests that some air stripping of these constituents may be occurring.

Small amounts of various chlorinated dioxins were found in the effluent (<340 ng/L, using method SW8280) and, particularly, the sloughed biomass sludge, where one sample did exhibit 1900 ng/g of OCDD isomer. This value is currently being re-examined. With one exception, an effluent sample found to contain 62 ng/L, the 2,3,7,8-tetrachlorodioxin of primary concern was not detected in any of the influent, effluent, or sludge samples using high resolution GC coupled with low resolution MS.

The incoming groundwater was found to contain low concentrations of several

of the heavy metals, including nickel (<91 ug/L), zinc (<32 ug/L), copper (<25 ug/L), lead (<11 ug/L), and arsenic (<6.5 ug/L) from the chromated copper arsenate wood preservative currently used in wood treatment at the site. With the exception of one sample which is believed to be an anomaly, there was no change in the concentrations of the metals across the system.

Acute biomonitoring with fresh water minnows (96 hr static test) and daphnia magna (48 hr static test) demonstrated that the toxicity in the incoming groundwater or the influent was essentially totally removed by the treatment. LC50's increased from an estimated low of 0.2% (groundwater/control water) for the groundwater to more than 100% (as calculated from results) in the treated effluent.

COSTS

Preliminary cost estimates were carried out by the vendor for operation of the pilot plant at MacGillis and Gibbs excluding the ancillary equipment such as carbon units and bag filter but including cost for nutrients, electricity, heat, labor and caustic. In addition, costs were extrapolated by the vendor to a full scale system capable of treating 30 gpm of a similarly contaminated (~40 ppm pentachlorophenol) groundwater based on the demonstration study and other information at their disposal. On these bases, operating cost at the 5 gpm and the 30 gpm rate would be \$4.24/1000 gallons and \$2.62/1000 gallons, respectively (Table 3). As shown in the table, certain costs do not increase at the expected rate. For example, unit nutrient cost would decrease because of bulk purchase; electricity cost/gallon treated decreases because it is assumed that with deeper bioreactor beds in the 30 gpm unit (8 ft instead of 4 ft) the energy for the compressor supplying the air would be used more efficiently; operator labor cost also are not expected to increase in direct proportion to the size of the unit.

TABLE 3. OPERATING COST OF TREATMENT (\$/1000 gal)

Cost Item	at 5 gpm	at 30 gpm
nutrients	0.042	0.017
electricity	0.416	0.216
heat	1.46	1.46
labor	2.08	0.69
caustic	0.24	0.24
TOTAL	4.24	2.62

These costs do not include leasing or amortization of the capital equipment, which are approximately \$3,200/month (5 gpm mobile), \$30,000 (5 gpm skid mounted) and \$80,000 (30 gpm skid mounted), respectively.

Clearly labor and heat (electrical) requirements are the major factors to consider when treating waters at a specific site. And, of course, any site-specific pre- or post-treatment requirements, such as oil/water separation, solids removal, polishing, air emissions control, etc., would have to be factored into the cost calculation for that site.

CONCLUSIONS

On the basis of the pilot plant study carried out at the MacGillis and Gibbs site in Minnesota, the BioTrol process would be successful in treating groundwater or other pentachlorophenol-contaminated wastewaters (at ~40 ppm pentachlorophenol) to levels suitable for discharge to a POTW or reuse within a plant. One unforeseen benefit of the treatment was that biotoxicity in the incoming groundwater was eliminated by the treatment.

Contaminated waters of different concentrations can be accommodated by increasing or decreasing the throughput rate, recycling a portion of the stream or by sizing the system differently. Site-specific factors such as groundwater temperature, ambient temperature, extent of contamination with oil and/or solids, etc., can all play a role in the cost-effectiveness of overall treatment.

Although a secondary objective of the study was to evaluate the effectiveness of the system for removal of polyaromatic nuclear hydrocarbons that might be present at the site as a result of the use of creosote, the levels of these constituents in the groundwater used for the study were too low to reach any conclusions as to removal.

FACTORS AFFECTING THE RELIABILITY
OF OPERATIONS OF THE EPA
MOBILE INCINERATION SYSTEM

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ABSTRACT

The EPA Mobile Incineration System has been operated, from October, 1985 until April, 1989 at the Denney Farm Superfund Site at McDowell, Missouri, to demonstrate the high-temperature incineration of hazardous wastes. These consisted of a wide variety of solids, liquids and sludges contaminated with 2,3,7,8-tetrachlorodibenzo-p-dioxin and other hazardous compounds. The system started with an availability of only 40% but achieved an availability of 80% during the site closure period. Based upon the operating experience, the availability of the system was determined by: the interaction of various parts of the system with feed or ash characteristics, basic mechanical design factors, crew shakedown periods at the start of each operating period, and interruptions to perform scientific and regulatory tests. This paper discusses the factors that determined the availability of the unit, the corrective actions taken to deal with adverse feed characteristics and design deficiencies, and the results of the corrective actions. The information contained in this paper is directly applicable to field use of mobile and transportable incinerators at Superfund and other industrial cleanup sites.

DISCLAIMER

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FACTORS AFFECTING THE RELIABILITY OF OPERATIONS OF THE EPA MOBILE INCINERATION SYSTEM

INTRODUCTION

Under the sponsorship of the Office of Research and Development of the U.S. Environmental Protection Agency (EPA), the EPA Mobile Incineration System (MIS) was designed and constructed to demonstrate high-temperature incineration of hazardous wastes [1,2,3,4,5,6]. The full scale demonstration of the unit occurred at the Denney Farm Superfund Site at McDowell, Missouri, from October, 1985 until April, 1989.

This paper presents an analysis of the factors affecting the reliability of the operations of the EPA Mobile Incineration System (MIS) during the above period. The reliability of the system is measured in terms of availability. Availability is defined as the actual operating time when feed was entering the system divided by the total time available for processing feed multiplied by 100.

The availability of the MIS was determined by several factors consisting of: the interaction of the various parts of the system with feed or ash characteristics, basic mechanical design factors, crew and equipment shakedown periods at the start of each operating period, and interruptions to perform scientific and regulatory tests. As the incineration of the contaminated materials progressed, adverse feed characteristics and deficiencies in the design and operation of the MIS were identified. Corrective actions were taken to deal with adverse feed characteristics and to remedy design deficiencies. These actions produced increases in the capacity and the reliability of the MIS and a significant reduction in operating costs. Figure 1 shows that the availability was increased from 40% to 80% between 1985 and 1989.

Correction of a major design deficiency or corrective actions to remedy problems due to adverse feed characteristics often did not show the anticipated increase in availability. Although a problem had been corrected by the changes to the unit, other problems would surface, and only a small increase in availability was obtained. This occurred because during the long downtimes caused by the original problem, maintenance was performed on the entire system. This general maintenance sometimes hid these other problem areas. Specific examples are discussed below.

Description of the MIS

The MIS, shown in Figure 2, consists of a refractory-lined rotary kiln, followed by a cyclone, a secondary combustion chamber (SCC), and an air pollution control system. The air pollution control system consists of a quench system, followed by a wet electrostatic precipitator (WEP), a packed bed

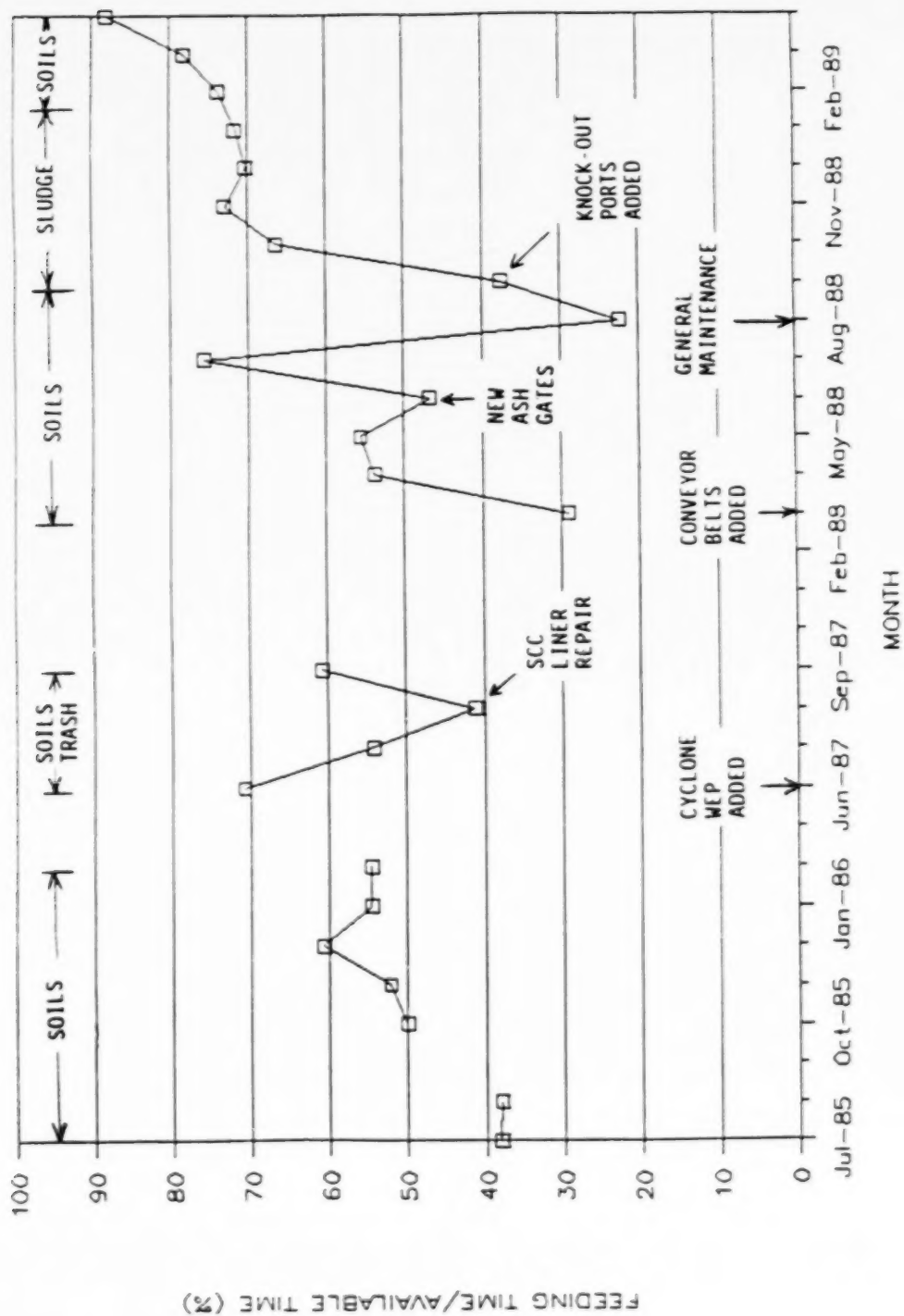


Figure 1. MIS availability.

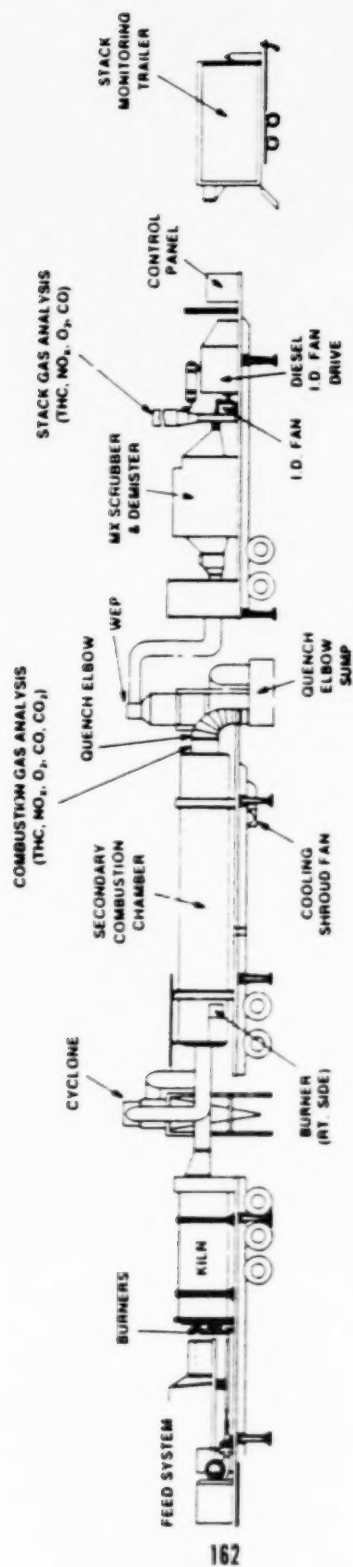


Figure 2 EPA Mobile Incineration System

scrubber and a mist eliminator [5]. Auxiliary systems consist of the feed handling, ash handling, and air pollution monitoring systems. The feed handling system contains a conveyor system, shredder, weigh scale, ram feeder, and HEPA/Carbon filtration system for fugitive dust and vapor control. The ash handling system has alternating gates to minimize air in-leakage into the back of the kiln. The ash is discharged into drums. The air pollution monitoring system contains instruments to continuously monitor oxygen and carbon dioxide and to periodically monitor carbon monoxide, unburned hydrocarbons, and nitrogen oxides.

AVAILABILITY DURING 1985-1986

During 1985 the overall availability averaged 50% while processing materials from the first five sites as shown in Table 1. The chief cause of downtime or unavailability was the buildup of solids in the SCC. Approximately 90% of the downtime was attributable to cleaning out the particulate carryover from the kiln to the SCC. Other sources of downtime were extensive maintenance on the Cleanable High Efficiency Air Filter (CHEAF) and feed system jams. The addition of the cyclone and the replacement of the CHEAF with the WEP were the major actions taken to address these concerns. The addition of the Linde "A" Burner System^R helped to reduce the amount of carryover that the cyclone had to handle by decreasing the kiln exit gas velocities. Table 2 shows that these changes were effective in solving these problems. Based upon the lost processing time for cleaning the SCC, the availability was predicted to increase to 80% if the above design changes were implemented.

AVAILABILITY DURING 1987

During the 14-week operation of the modified system, an overall system availability of 53% was achieved. This consisted of a 30.5% availability during the trial burn and a 54.8% availability during other activities.

Although slagging or plugging of the SCC was almost eliminated, the anticipated improvement in availability did not materialize. New sources of downtime or unavailability were encountered. The new causes of downtime were the slagging of the kiln that accounted for 10.6% and delays caused by testing and preparation for testing that caused 8.7%. Other important factors were mechanical failures accounting for 9.9% and human error accounting for 7.4%. The causes of downtime are presented in Tables 2 and 3. The reasons for these periods of unavailability are discussed below.

Kiln Slagging

Kiln slagging became a factor in 1987 due to the processing of large quantities of trash that constituted about 40% of the feed to the MIS. The trash present in the feed caused slagging of the kiln walls with a lava-type hard material that eventually built a dam restricting the flow of material through the kiln. This dam was located at about eight feet from the front or at the midpoint of the kiln. The materials conducive to the slagging were

TABLE 1. MIS OPERATIONS SUMMARY

Feed Source or Activity	Date of Activity	Pounds Processed		Avail. ¹ (%)	Hours Out	Hours Online	Total Hours
		lb Solids	lb Liquids				
1985-1986							
Neosho and The Farms ²	7/23/85-8/27/85	436,000	60,300	38.1	591	363	954
Neosho and The Farms ²	10/26/85-2/03/86	<u>1,495,000</u>	<u>107,300</u>	54.0	1313	1540	2853
1985-1986 Totals		1,931,000	167,600	50.0	1904	1903	3801
1987							
Neosho and The Farms ³	6/12-9/18	1,095,000	31,300	54.8	995	1217	2212
RCRA/TSCA Trial Burn ⁴	7/28-8/3 8/31-9/1	<u>162,000</u>	<u>7,600</u>	30.5	132	58	190
1987 Totals		1,257,000	38,900	53.1	1127	1275	2402
1988-1989							
Baldwin Park ⁵	2/22/88-4/27/88	911,000	22,200	39.1	966	620	1586
Baldwin Park Trash ⁶	8/02/88-8/12/88	136,000	3,800	58.9	104	149	253
Brominated Sludge Tests	4/28/88-5/01/88	49,000	0	55.1	35	43	78
Verona	5/02/88-8/01/88	3,097,000	3,000	59.8	891	1324	2215
Maintenance	8/12/88-8/31/88	0	0	0.0	0	0	0
Brominated Sludge	8/31/88-1/23/89	2,161,000	1,400	60.8	1331	2061	3392
Closure ⁷	1/24/89-4/15/89	<u>2,989,000</u>	<u>200</u>	80.0	382	1530	1912
1988-1989 Totals		9,343,000	30,600	60.7 ⁸	3709	5727	9436
1988-1989 Totals w/out sludge ⁹		7,182,000	29,200	60.6 ⁸	2378	3666	6044
Totals for 1985-1989		12,531,000	237,100				
GRAND TOTAL			12,768,000				

1. % Availability = (Time Processing Solid Feed/Total Time) x 100.
2. The Farms are Denney, Erwin, Rusha and Tally. Only small quantities of trash were processed.
3. Included is approximately 475,000 lb of trash.
4. The low availability was due to preparation time and a failed kiln bearing.
5. The low availability was due to problems encountered during the start-up in February and March, 1988.
6. Most of the material was trash consisting of wooden pallets and steel drums with some soils.
7. Due to Decontamination of the feed system the records stop on April 16. Incineration activities continued until April 22, 1989, chiefly on residues from cleaning the feed system.
8. Availability calculation excludes the August, 1988 maintenance period.
9. These data represent the operating summary for soils only in 1988-1989.

TABLE 2. DESCRIPTION OF PROBLEMS ENCOUNTERED DURING THE OPERATION OF THE MOBILE INCINERATION SYSTEM, CORRECTIVE ACTIONS TAKEN, AND THE RESULTS OF THE CORRECTIVE ACTIONS

Year	Problem	Cause	Corrective Action	Result	% Availability Lost Before	% Availability Lost After
1985/1986	Secondary Combustion Chamber (SCC) Plugging	Particulate Carryover from Rotary Kiln	Cyclone & Oxygen Burner - 1987	Plugging of SCC Solved	44	0.6
	Cleanable High Eff. Air Filter (CHEAF)	Mechanical Problems	Wet Electrostatic Precipitator (WEP) & CFI Separator - 1987	Reduced Maintenance	3.5 ¹	1.5
	Feed System Ram Jams	Buildup on Back of Ram	Hauptman ^R Conveyor - 1987	Reduced Frequency	2.6 ¹	1.3
1987	Feed System	Blockages at Doctor Blade	Roller Dam - 1988	Easier to Keep Clear	Affected Throughput	
	Feed System	Bridging of Wood & Steel Drum Rings	Television & Manual Size Reduction - 1988	Reduced Frequency and Quicker Response	Affected Throughput	
	Kiln Slagging	Trash Feed	Reduce Kiln Temp. Blend Trash with Soil - 1987	Reduced Frequency	10.6	NA ²
	Process Water Contamination	Human Error	Change Operating Procedures	No Recurrence	7.4	0

(continued)

¹ est. = estimated

² NA = not applicable. The ash gate problem obscured any comparison. The 5% unavailability was encountered after the ash gates were repaired.

TABLE 2. (Continued)

Year	Problem	Cause	Corrective Action	Result	% Availability Lost Before	% Availability Lost After
1986	Kiln Stalling	Air Leakage Past Ash Gates	Redesign Ash Gates	Greatly Reduced Frequency	16.8	5.0
1987	SCC Exit Venturi	Acid Gas Corrosion (HCl)	Use Haynes ^R Alloy 525	Three month life	6.3	5.3
1988	SCC Exit Venturi	Acid Gas Corrosion (HCl)	Use Castable Ref.	No problems after 9 mo.	5.8	0
1987/1988	MEP Rod Problems	Frequent Shorting	Stainless Steel Brace internals	No rod failures after 7.5 mo.	4.6	4
1988	Process Water Pipe Corrosion	pH swings	Redesign pH control and caustic injection system	Improved pH control Insufficient time to evaluate corrosion	5.0 ¹	4
	Stack Monitoring	OD meter, New Crew	New OD Monitor & Training	Good performance over 13 months	9.5 ³	1.4
	Rotary Kiln to SCC Duct Fouling	Brominated Sludge Ash	Install knockout ports	Allowed Hot Cleanouts	15.	9.4
	Compressor Failures	Loss of Fuel due to Insufficient Head	Use recirculating pump	Prevented loss of diesel	1.6	0
1985-1988	Miscellaneous Failures	Wear and Tear on unit	Ascertain & stock critical spare parts	Reduced waiting time for repair parts	5-10	2-3

³ Unavailability expressed as time lost during the Baldwin Park incineration activity.

TABLE 3. CAUSES OF SYSTEM UNAVAILABILITY IN 1987

Cause	Unavailability (%)
Kiln Slagging	10.6
Mechanical	9.9
Testing Delays	8.7
Human Error	7.4
WEP	4.6
Feed Jamming	3.5
Electrical	<u>2.3</u>
Total	47.0

plastic materials used to contain the contaminated dirt during transport to the site and the discarded clothing and material used during cleanup, such as rubber gloves, plastic suit material, boots, etc.

During 1987, the chief methods of minimizing slagging of the kiln were to operate the kiln at the lowest feasible temperature, about 1450°F or 50°F above the low temperature feed cutoff setting, and to blend as much contaminated soil as possible with the trash.

Prior to the modifications only small quantities of trash had been fed because of the difficulties encountered in processing it. Processing difficulties included inability to control kiln temperature and excess oxygen, and feed system jams [7,8]. The modifications to the feed system and the addition of the oxygen burner system permitted the feeding of trash but slagging of the kiln then became a major reliability factor. Slagging is caused by the presence of sodium and potassium in the ash. The mechanism of slagging is discussed further in References 9 and 10.

Trash content of the feed also was a major causative factor for the 3.5% unavailability due to feed jamming. The trash often jammed at the doctor blade or restricting dam that was originally used to level the granular material on the conveyor belt. The doctor blade worked quite well for granular material but it created large blockages when materials such as shredded plastic, clothing, trash, metal, or mud were fed. As shown in Table 2, a roller was installed to replace the doctor blade and this reduced the number of jamming incidents.

Testing Delays

Delays related to testing accounted for 8.7 % unavailability [11]. These delays were associated with times required to clean out the system (kiln, conveyor, water system flush, etc.); to prepare for tests; to hold the system on hot standby between tests; and to perform special calibrations. About 25% of the unavailability related to testing represents the downtime during the Demister^R installation. The installation of this mist eliminator was required to prevent high particulate emissions when the unit was processing feeds containing percent levels of organic chlorides. This situation was encountered during the 1987 trial burn [4].

SCC Venturi Failures

The failure of the Inconel^R 625 venturi at the exit of the SCC caused 6.3% downtime as shown in Table 2. This accounted for most of the mechanical sources of downtime. After over 3000 hr of operation, some of which was with highly chlorinated compounds, the exit venturi had completely disintegrated, and its support plate showed severe stress corrosion cracking. Based upon the presence of chlorine in conjunction with the high temperature (2200°F), the material for the venturi and diffuser was changed to Haynes^R alloy 556. The change to this material failed to extend the life of these parts. A venturi, fabricated from castable refractory, was installed during the summer of 1988. This refractory venturi was in excellent shape after 9 months with over 5000 hours of operations when the MIS activity at Denney Farm was completed.

Human Error

Human error caused 7.4% of the unavailability. This consisted of the time to decontaminate the process water system when it became contaminated with furans. System downtime caused by contamination/decontamination of equipment is an added cause of unavailability in hazardous waste operations. This source of downtime is not normally encountered in equipment processing nonhazardous materials.

The furans release occurred in the following manner. The kiln rotation was stopped during Test 4 of the trial burn due to the kiln bearing failure. After the kiln rotation was stopped, the operators manually shut down the entire system. This action stopped the kiln burners, the SCC burners, and the ID fan. The ID fan was quickly restarted because of the puffing from the kiln but the SCC burners were not restarted. Failure to restart the SCC burners was a critical error because this created a rapid drop in the SCC temperature. This temperature drop caused generation of furans due to incomplete combustion of PCBs which continued to volatilize from the solid waste remaining in the kiln. Consequently, these furans contaminated the process water system as shown by their presence in both the process water sample taken prior to Test 5 and the water samples taken during Test 5. Some of these furans then were released from the stack during Test 5.

The contamination of the process water system was not discovered until after Test 5 had been completed the following day. At this point, further trial burn testing was postponed and normal operations were continued until it was pointed out that they should be stopped in order to decontaminate the process water system.

The primary lesson learned from this experience is that should the kiln rotation be stopped with contaminated solid materials in the kiln, the SCC burners must continue to operate. The operators were instructed to keep the SCC burners on whenever the kiln rotation was stopped. If the SCC burners should trip, they should be relit following proper procedures including an air purge. A second lesson learned from this experience is that if ever there is any indication that an incident has contaminated the process water, the system operation should be terminated because of the potential for the release of contaminants from the stack. The process water should be analyzed to determine if contamination has occurred, and then be completely decontaminated if necessary.

Risk Analysis

Since a release of furans is potentially harmful to the surrounding population, a risk analysis [4] was conducted to determine the impact of the furans release. The risk analysis was conducted using state-of-the-art methodology and in accordance with EPA procedures. In addition, the risk analysis always assumed a "worst case scenario". The results showed that the incident was minor. There was no additional risk to the public resulting from the incident.

WEP Problems

The WEP caused 4.6% downtime as follows: It was difficult to establish the required high voltage during initial startup of the precipitator. The electrodes had to be positioned accurately within each box cell before voltage could be sustained without breakdown. After a hot cycle, the WEP again failed to hold high voltage because of electrode shorting. The electrodes were again adjusted and reinforcing angles were added to the rod suspension system. The unit performed normally for 20 days, and then all three circuit boards failed in the control panel catastrophically. This caused a three-day shutdown until new replacement circuit boards could be installed. No conclusive reason could be established for the failure, but metal chips from the initial cabinet assembly were thought to be the cause. After replacing the boards and turning off the fogging sprays, the unit sustained satisfactory operation. It has been necessary to perform a wash cycle daily or more often in heavy feed conditions to maintain high voltage. This wash cycle removes particulate buildup from the surfaces of box cells.

The fiberglass rods also were subject to a rupture failure mode that occurred after repeated short cycles. The shorting happened usually during startups after a shutdown of the MIS. This shorting is attributed to movement of the rods due to expansion and contraction as the equipment warms and cools. To overcome both the rod movement problem and the rupture failure problem, the rod material was changed to Type 304 stainless steel. The stainless steel rods were installed in the unit during September 1988. They solved the rupture problem but periodic shorting still occurred.

AVAILABILITY DURING 1988 AND 1989

During 1988 and 1989, the availability of the unit averaged 61%. This period was marked by constant improvement in the availability, because many problem areas such as the SCC venturi nozzle, the kiln ash gates, the WEP rod failure problem, the pH control system, the diesel fuel delivery system and the spare parts inventory were addressed. As shown in Figure 1, availability of the MIS exceeded 70% from November 1988 until the end of Closure - a period of 6 months. The 70% level was exceeded even when the unit was processing brominated sludge, which was difficult to handle because its ash tended to foul flue gas passages and instruments. The Closure period was marked by a record 80% availability.

Kiln Ash Gates

The kiln downtime was caused mainly by slagging. The ash gates were discovered as a source of the slagging in June, 1988 as follows. During June the rate of slagging had increased, and the kiln caused 37% MIS downtime. Fuel flowrates to the kiln also had increased. Inspection of the ash gates during troubleshooting of the problem showed that they had warped and did not close properly. The failure to close permitted excessive air leakage that cooled the flue gases at the exit of the kiln. Since the control thermocouple for the

kiln was downstream of the leakage point, it read an estimated 300°F to 400°F lower than the average gas temperature in the kiln. This caused the kiln burners to fire harder to achieve the setpoint temperature. Consequently, the kiln operated several hundred degrees higher than required.

Inspection of the ash gate design showed that it could be improved to provide tighter closure. A new design was installed. Following installation of the new ash gates, the lost time from kiln slagging, which had averaged 16.8% during the first half of 1988, dropped to 5% as shown in Table 2.

pH Control Improvement

During 1987 the MIS experienced difficulty in controlling the pH in the process water system. Corrosion in the process water system was attributed to excursions when the process water became acidic for brief periods of time. The pH control was improved in stages starting with changes in 1987. The nature of the problem and the steps taken to solve it are described below.

The scrubber system for the MIS utilized a caustic solution to neutralize the HCl gas formed and to maintain the scrubber water pH in the 7 to 9.5 range. There were three areas in the MIS where the flue gas was scrubbed:

- Quench elbow and sump
- Lower WEP filler region
- Mass transfer (MX) scrubber

A 10% to 20% caustic solution was injected into the quench sump and into the recirculation water flow of the MX scrubber. The initial and largest percentage of the neutralization occurred in the quench elbow and sump. For that reason the majority of the caustic had to be injected at this location. The injection of caustic directly into the quench system tank from a line controller by a solenoid valve located 25 feet upstream caused large swings in the pH (3-10.5) of the quench sump. The long injection line between the valve and the quench sump caused a delay in caustic injection after the valve was activated. The pH continued to decrease during this delay. After the valve was closed, the line caused an uncontrolled trail-off of injection. The pH continued to rise during the trail-off. The swings could be controlled for any one condition of organic chloride loading by changing the setting of the timer. However, when organic chloride loading changed sharply, the timing required manual changes. Also, under heavy loadings the swings were still excessive. In 1987, the caustic injection valve was placed at the quench sump to eliminate the delays. This reduced the uncontrolled swings but did not completely solve the problem. Further steps were necessary as described below.

The pH was controlled with pH sensors which operated in slip streams from the recirculation water loops. These sensors fouled easily and required frequent cleaning to keep them functional. Also, the sensors were suitable for only on/off control of the caustic solution.

In 1988, the system was changed to modulating control using a Great Lakes[®] unit, which also featured a flow-through sensor. This change produced

smooth control of the pH, and the flow-through sensors were resistant to fouling. Hence, control was improved and maintenance on the instrumentation and the process water system was decreased.

Spare Parts Inventory

During 1988, a study was performed which identified critical spare parts. The study was conducted by maintenance experts who checked the operating requirements, the equipment manuals, and added their own experience to produce a list of critical spare parts. These parts were purchased and put into inventory. The spare part inventory prevented the downtime that was sometimes associated with waiting for a critical spare part to arrive. This arrangement could save anywhere from a few hours to one or two days of time depending upon the availability of the failed part.

Fouling

The fouling consisted of: deposits that restricted the flow areas in the duct system, the cyclone, and the quench elbow; deposits that fouled the thermocouples, the kiln oxygen analyzer, and other instrumentation; and sedimentation that filled the quench sump and the CPI separator. The rate of fouling was highly dependent on the ash characteristics of the feed materials [9,10,12]. The ash from brominated sludge, which contained calcium and sulfur, formed a consolidated deposit which fouled the ductwork between the kiln and the SCC. A consolidated deposit also occasionally formed in the quench elbow upstream of the quench nozzles. This fouling necessitated a system shutdown about every twelve days to remove the deposits.

For brominated sludge, fouling caused 9.4% downtime (320 hr) but for most feed materials fouling was controlled by the cleaning of the system during general maintenance periods. The installation of clean out ports in the duct system was a necessary action to minimize the downtime caused by the ash from brominated sludge.

Instrument Problems

Instrument problems accounted for 2.9% downtime. These consisted of instrument failures such as the CO analyzer failure, weigh scale failures, broken thermocouples, etc. Instrument problems were highest immediately after start-up during the Baldwin Park campaign. Instruments contributed 10.3% downtime (163 hr) during this period. Much of this downtime (88 hr) was caused by failure of the CO analyzer and computer problems in the analytical trailer. After the Baldwin Park campaign, instrument problems occurred when the unit was processing difficult feeds such as brominated sludge or trash. When the unit was processing soil, instrument problems were minimal.

PROBLEM SUBSYSTEMS

The systems viewpoint of availability shows which part of the MIS contributed most to the downtime. As shown in Table 4, problems associated

with the kiln produced the greatest downtime during 1988-1989. The 12.9% downtime accounted for about 30% of the total MIS unavailability. Most of the downtime associated with the kiln was due to slagging. This is shown in Table 5. The second largest category was downtime that affected the total system. These included periods for general system maintenance and the testing periods. The 7.7% downtime affecting the total system accounted for about 18% of the unavailability. The duct system caused 5.3% downtime, which accounted for about 13% of the unavailability. The duct system downtime was caused almost entirely by fouling by ash from the brominated sludge. The SCC caused 5.1% downtime, which accounted for 12% of the unavailability. The SCC downtime was evenly divided between refractory repairs and the repair of the corroded metal venturi. A small percentage was caused by fouling. The feed system caused 3.9% downtime, which accounted for 9% of the unavailability. This was mainly caused by conveyor problems.

CONCLUSIONS

The paper has discussed the factors that affected the availability of the MIS during the operations at Denney Farm; has shown how the areas which caused downtime were identified and addressed; and has presented the results of the actions taken to improve availability. The conclusions based upon the operating experience are presented below:

- o By analyzing and correcting problems, the availability of the MIS was increased from 40% to 80%. During the last 6 months of operation, availability exceeded 70%.
- o Horizontal SCCs can become quickly plugged by carryover of particulate matter from the kiln. A cyclone placed between the kiln and SCC is effective in preventing this problem.
- o Kiln slagging caused a significant percentage of the downtime. Kiln slagging can be minimized by operating the kiln at minimum feasible temperatures, by blending slag-forming feed materials with large quantities of nonslagging feed materials, and by insuring accurate temperature readings to prevent overfiring. Prevention of cold air leakage upstream of a control thermocouple is very important to prevent slagging.
- o When processing hazardous wastes, inadvertent contamination of clean parts of the system can be an added source of equipment downtime.
- o Refractory materials were able to withstand the combination of high temperatures ($>2000^{\circ}\text{F}$) and high hydrochloric acid concentrations much better than high nickel alloys.
- o Control of pH is important to prevent corrosion of the process water system. Although the downstream end of the air pollution control system remained basic, other parts of the system periodically became acidic. This caused corrosion in these parts of the system.

TABLE 4. SYSTEM SOURCES OF MIS UNAVAILABILITY
1988-1989

Feed Source or Activity	Cumulative Downtime by MIS System Expressed as % Downtime										Total Unavail.
	Instr. Air	All	APC	Ash	Ducting	ID Fan	Feed	Kiln	Quench	SCC	
Baldwin Park	0.06%	2.27%	9.52%	0.57%	0.00%	0.00%	7.69%	28.75%	0.69%	11.35%	60.91%
Baldwin Park Trash	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	1.58%	39.53%	0.00%	0.00%	41.11%
Scoping Burn	0.00%	55.13%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	44.87%
Verona	0.09%	6.68%	0.41%	0.63%	0.00%	5.51%	6.85%	30.23%	0.60%	9.79%	40.23%
Maintenance	0.00%	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%
Brominated Sludge	4.35%	0.68%	1.36%	0.21%	12.91%	1.87%	1.45%	10.18%	3.23%	3.17%	39.40%
Closure	0.37%	3.45%	0.00%	0.05%	4.71%	0.00%	7.27%	2.56%	0.00%	1.57%	19.98%
Average by System	1.59%	7.69%	2.08%	0.31%	5.31%	1.87%	3.92%	12.91%	1.28%	5.08%	

Note: The selection of the causes of unavailability are dependent on engineering judgement. This adds a degree of uncertainty. The maintenance period caused an unavailability of 5% which included the WEP rod replacement, system cleanouts, etc.

TABLE 5. SOURCES OF MIS UNAVAILABILITY BY TYPE AND PERCENTAGES
1988-1989

Feed Source or Activity	Mech.	Feed Jamming	Ash Jamming	Cumulative Downtime %					Slagging SCC	Testing	Maint.	Fouling
				Elect.	Human	Slagging Kiln	Instr.					
Baldwin Park	28.80%	0.25%	0.25%	2.65%	2.21%	16.33%	10.28%	0.06%	0.00%	0.00%	0.00%	0.00%
Baldwin Park Trash	0.79%	0.40%	0.00%	0.00%	0.00%	37.55%	2.37%	0.00%	0.00%	0.00%	0.00%	0.00%
Scoping Burn	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	44.87%	0.00%	0.00%	0.00%
Verona	14.04%	0.00%	0.00%	0.54%	0.99%	17.16%	0.90%	0.00%	0.00%	0.00%	6.59%	0.00%
Maintenance	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	100.00%	0.00%	0.00%
Brominated Sludge	8.28%	0.59%	0.03%	1.74%	0.18%	8.11%	2.71%	1.68%	0.00%	0.00%	6.49%	9.43%
Closure	7.01%	2.41%	0.00%	0.58%	0.00%	0.00%	0.42%	0.00%	0.00%	0.00%	3.40%	6.17%
Average by Type	11.99%	0.72%	0.05%	1.25%	0.63%	10.20%	2.92%	0.59%	0.35%	8.94%	4.43%	

- o An adequate spare parts inventory is important to minimize downtime associated with obtaining parts which are not available onsite.
- o Adverse feed characteristics can cause internal fouling of ductwork. An incineration unit should be equipped with an ample number of cleanout ports to facilitate cleanout.
- o Failures in the monitoring system required by the operating permit is another added source of downtime.
- o Correction of a problem that is causing significant periods of downtime does not insure large increases in system availability. The problem may be replaced by another problem which is kept under control by maintenance when the system is down.

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**CHARACTERIZATION OF INTERNAL INSPECTION PROCEDURES
& EQUIPMENT FOR UNDERGROUND STORAGE TANKS**

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ABSTRACT

Efforts are presently underway to examine the various tools and techniques used for conducting internal inspections. This study documents the significant factors that are evaluated during an inspection. It examines the application of each inspection method by identifying the procedural steps, necessary equipment and instrumentation involved, and the circumstances under which the method is performed. This paper presents an overview of the inspection methods currently being used by practitioners.

INTRODUCTION

IMPETUS FOR THE STUDY

Releases from underground storage tanks (USTs) are increasing in number nationwide. Internal inspections fulfill an important role in the repair, maintenance, and release prevention of USTs. Existing inspection methods and techniques range from visual inspection to ultrasonic and magnetic testing. A common inspection method, for example, involves striking a ball peen hammer on the interior wall of a tank and making a determination on its thickness based on the ringing sound produced. The U.S. EPA's Risk Reduction Engineering Laboratory is presently directing a project to characterize internal procedures and equipment for performing internal inspections of USTs. In this study, the technical applicability of these different inspection techniques, in light of the UST regulations, was investigated.

While the Federal regulations recommend internal inspection procedures developed by nationally recognized organizations, such as the American Petroleum Institute (API) and the National Leak Prevention Association (NLPA), for use in repair or upgrading of USTs (40 CFR 280.33 and 280.21, respectively), internal inspections are performed for other reasons. These circumstances include: structural integrity evaluations, tank reconditioning, tank closure, and change-in-service. In addition to the types of internal inspection referenced in the regulations, many others have been developed by tank manufacturers and engineering societies and are in various degrees of use.

PROJECT OBJECTIVES

This study identifies and characterizes current techniques used for conducting internal inspections of underground storage tanks. The study investigated state-of-the-art (SOTA) for internal inspection methods. The term 'state-of-the-art' is defined as the

current level of development and capability in terms of procedure, process, and technique in current practice. This study includes a review of existing industry standards and practices. It also contains a review of non-destructive test methods.

APPROACH

The research effort associated with this study consisted of a review of available literature and conversations with trade and professional associations, manufacturers, vendors, and independent consultants. No sampling or analyses was performed in conjunction with this study. No direct observation of procedures has been undertaken.

LITERATURE SEARCH

An extensive review of current literature related to internal inspection of storage tanks utilized both computerized literature data bases and hard copy documents found in engineering and technical libraries at various universities and the EPA. In general, little information on internal UST inspections was available. Detailed documentation on several types of inspection equipment, however, was obtained from non-destructive testing handbooks and ASME Boiler And Pressure Vessel Code.

CONTACTS WITH PROFESSIONAL ASSOCIATIONS

Professional and trade associations were the most valuable source of information on SOTA practices. Types of information gathered included: general descriptions of the procedures and the steps involved in performing them, examples of the instruments used to conduct the inspection, and details on method performance. Some basic information on field considerations (such as permitting requirements, portability of equipment, cost to perform the inspection and any special considerations for waste generated during

the inspection) was also collected. The organizations contacted are presented here:

- Petroleum Equipment Institute (PEI)
- American Petroleum Institute (API)
- Steel Tank Institute (STI)
- National Leak Prevention Association (NLPA)
- Fiberglass Petroleum Tank & Piping Institute (FPT&PI)
- National Association of Corrosion Engineers (NACE)
- American Society of Testing & Materials (ASTM)
- Association of Composite Tanks (ACT)
- Non-Destructive Testing Association (NDTA)
- American Society of Mechanical Engineers (ASME)

CONTACTS WITH MANUFACTURERS, VENDORS & CONSULTANTS

Representatives of the industries which manufacture tanks, apply linings, or provide inspection services were contacted to obtain details on particular inspection methods. Among the field from which information was obtained are: Owens-Corning (an FRP tank manufacturer), Buffalo Tank Company (manufacturer of steel tanks), (Bridgeport Chemical Company (a manufacturer and installer of lining resins). Conversations with these representatives focused on the identification of procedures and equipment currently in practice. Information on potentially applicable or emerging internal inspection methods and procedures was also gleaned from these discussions.

REVIEW OF APPLICABLE STANDARDS

Since the regulations rely on existing inspection methods, efforts also focused on investigating standards relevant to UST inspections. No single standard describes procedures for all types of internal inspections. Current standards cover activities performed during the installation and upgrading of tanks. Inspection procedures relating to UST design and construction have been developed by tank manufacturers as part of their quality

assurance/quality control protocols. In general, these serve as pre-installation requirements. Closure- and cleaning- oriented inspections have only been marginally addressed in the survey of information.

API Recommended Practice 1631, Internal Lining of Underground Storage Tanks

This recommended practice describes requirements and procedures for the application of lining material to the interior of existing underground petroleum storage tanks.

NLPA Standard 631, Internal Inspection, Repair and Lining of Steel and Fiberglass Storage Tanks

This standard creates specific requirements to evaluate the appropriateness of issuing a permit to perform internal inspections and provides criteria to evaluate the lining materials used.

NLPA Standard 632, Internal Assessment of Steel Tanks 10 Years and Older for Corrosion Holes and Structural Soundness

This standard provides the minimal internal inspection procedures to obtain accurate assessment of the structural soundness and the amount and level of corrosion prior to installing a corrosion protection system.

ACT 100, Specification for The Fabrication of FRP Clad/Composite Underground Storage Tanks

This standard provides guidelines for the fabrication of FRP clad/composite underground storage tanks that meet UL58 "basic tanks" standards.

FPTPI Recommended Practice-T-89-1, Remanufacturing of Fiberglass Reinforced Plastic Underground Tanks

This recommended practice addresses the accepted practices by the FRP industry for remanufacturing of fiberglass reinforced tanks.

Underwriters Laboratory Standard 1316, Glass-Fiber-Reinforced Plastic Underground Storage Tanks for Petroleum Products

This recommended practice is designed for fiberglass-reinforced plastic (FRP) USTs to contain petroleum products that are covered by UL.

STUDY FINDINGS

OVERVIEW OF INTERNAL INSPECTION METHODS

Eighteen methods have been identified during the course of this study and are listed in Table 1. Telephone discussions imply that only a few of these methods are actively in use as current practice (visual observation, hammer testing). Many others are applied infrequently throughout the country. In addition, our research has identified a few technologies (e.g., acoustic emission) as being speculative for internal UST inspection applications.

UST ACTIVITIES INVOLVING INTERNAL INSPECTIONS

Internal inspections fall into one of several categories depending upon the activity being performed on the UST. These inspections are conducted during installation, routine maintenance, repair, lining, change-in-service, or closure. In addition, many tank manufacturers (both steel and FRP) have instituted stringent in-house internal inspection procedures at various stages of the manufacturing process. Some states now require inspections by state UST personnel or certified inspectors at the time tanks are closed.

Table 1. Distribution of Internal Methods By Type of Activity and Tank Material

METHOD	INSTALLATION		UPGRADING		CLOSURE		REMANUFACTURING	
	STEEL	FRP	STEEL	FRP	STEEL	FRP	STEEL	FRP
TANK DISCONTINUITIES								
Visual (Human Eye)	X	X	X	X	X		X	X
Visual (Boroscope) *			X	X			X	X
Liquid Dye Penetrant			X	X			X	
Magnetic Particle			X	X			X	
Eddy Current **			X	X			X	
Radiography **			X	X			X	
Acoustic Emission *			X	X			X	X
Microwave *			X	X			X	X
TANK TIGHTNESS								
Bubble Test	X	X						X
Pressure Change	X	X					X	X
Vacuum Test	X	X						X
TANK THICKNESS								
Ultrasonic			X	X			X	X
Hammer Testing								
TANK LINING								
Holiday Test			X	X				X
Lining Hardness Test			X	X				X
Dry Film Thickness			X	X				X
TANK DEFLECTIONS								
Internal Tank Diameter		X						
TANK CONTAMINATION								
Tank Cleaning			X	X	X	X	X	X

* Emerging technologies

** Applicable technologies not practiced

Installation inspections are designed to identify any structural damage immediately after the tank is in place and to check tank tightness. Upgrading inspection activities are designed to evaluate: tank lining, tank discontinuities, tank wall thickness, and tank deflection. Inspections at closure assist in ascertaining the level of cleanliness before removal or abandonment-in-place. A new element in internal inspections is the remanufacture of tanks that have been taken out of service. This is a very new and rapidly evolving business area and information is still being collected.

METHODS IN ACTIVE PRACTICE

Visual Inspection

This method is used to detect any surface discontinuities such as cracks and other porosities in both steel and FRP tanks. It may also be used to determine the subsurface conditions of an FRP with the use of other instruments. The quality of the inspection is primarily affected by lighting conditions in the tank and the experience of the inspector. Visual inspection is an inexpensive, quick method of evaluation but requires tank entry. It does not enable the inspector to detect small surface or subsurface discontinuities.

Liquid Dye Penetrant

This simple, non-destructive test is performed to detect discontinuities (such as cracks, pits or delaminations) on the surface of steel or FRP tanks. A liquid penetrant is applied to a cleaned tank surface and allowed to be absorbed by capillary action into discontinuities. A developer is then applied to draw the penetrant out of cracks. Depending upon the type of penetrant used, the resulting indications are visible under normal or ultraviolet light. The accuracy of the inspection method is heavily influenced by the presence of any contaminants which may interfere with the penetrant process. This method is also susceptible to moist or high humidity conditions which can inhibit the capillary action.

Magnetic Particle Test

This method uses an induced magnetic field in a localized area of the tank surface as a magnetic powder is applied. The flux leakage created by a surface discontinuity will attract the magnetic powder and result in a visual indication. ASTM has described a standard practice for the performance of magnetic particle tests. Reliability of the results is dependant upon the direction of the magnetic field and false indications may result if magnetization is too high. This is a non-destructive test for the interior surfaces of steel tanks which is most effective in detecting discontinuities on the surface of the tank. The requisite equipment is relatively small and versatile for field applications.

Bubble Testing

The principle of a bubble test is to locate a leak by applying a solution that will form bubbles when a gas passes through it. If no continuous bubble formation is observed, the UST is considered acceptable. Surface tension of the bubble solution must be sufficiently low to allow for the detection of small holes. Particular attention is given to tank seams and openings (such as unused ports). Bubble tests can be performed using either direct pressure or a vacuum. Direct pressure tests are more common.

Pressure Test

A positive pressure test involves the introduction of a known pressure of air or other ambient gas to the tank after all ports of entry have been sealed off. In order for the tank to pass the test, it must hold a designated level of pressure for a prescribed period of time.

Vacuum Test

A negative pressure test may be performed using the principles described for the positive pressure test in reverse fashion. After all ports of entry have been sealed, air is withdrawn from the tank until a specified negative pressure inside the tank is achieved. If the tank maintains this pressure over a designated period of time, it passes the test.

Holiday Tests

Holiday detectors are used to ascertain the presence of discontinuities such as voids, cracks, thin spots, foreign inclusions, or contamination in the coating film. The principle of the test is to connect an electromagnetic sensitive relay or solid-state electronic relay circuit that energizes an audible or visual indicator. A voltage detector (low and high voltage equipment is available) is employed according to the thickness of the lining.

Lining Hardness Test

This test is performed to verify whether an applied protective coating film has cured to a hardness that meets the manufacturer's specifications. An ASTM standard has been developed for the determination of indentation hardness of both reinforced and non-reinforced rigid plastics using a Barcol impressor. This device distributes force, using a hardened truncated steel cone, to determine the lining hardness in a steel tank. The method is fully portable and should not generate a hazardous waste or require additional safety considerations beyond those associated with tank entry.

Dry Film Thickness Measurement

In this method, an elcometer measures the thickness of non-ferromagnetic coating films including paint, electroplating, galvanizing, powder, plastic, and rubber applied to a ferromagnetic base. This instrument can be used to gauge the thickness of steel tank coatings. Overall accuracy of the procedure is high; small errors may arise from inconsistencies in the surface profile or the substrate material. There is no standard procedure for this instrument.

Ultrasonic Testing

This method may be used to determine the wall thickness of a steel or FRP UST and may also detect any surface or subsurface discontinuities. In this method, an ultrasonic wave is induced at the surface of the tank which propagates through the wall. The wave travels through the tank medium at a constant velocity dependent upon the physical properties of the tank. The wave is reflected back to the instrument when it encounters a discontinuity or wall boundary. The transient time of the wave is measured by a pulse-echo instrument to calculate the wall thickness. ASTM delineates

objectives for performing the test. API 1631 indicates that ultrasonic measurements are used for UST inspections, but provides no guidelines for its application.

Hammer Testing

In this method, an inspector strikes a brass hammer against a cleaned tank surface. The vibration and rebound of the hammer and the sound produced is dependent upon wall thickness. There is no proven method available to evaluate the effectiveness of hammer testing. This is considered a non-destructive test for steel tanks which can be performed quickly at relatively low cost. It is imperative, however, that an experienced inspector be engaged to obtain the most accurate results. Both API 1631 and NLPA 631 describe hammer testing in varying levels of detail.

Internal Tank Diameter

Precise measurements are taken and a series of calculations are performed to compute the internal diameter of the tank. From these calculations, it can be determined whether or not the tank has been deflected and by what amount (percent). Some standards require no greater than a 1% deflection to ensure structural integrity of the tank.

Table 2 depicts the various circumstances under which internal inspections are performed and the types of tanks for which the method is appropriate. Throughout the course of the study, two methods were identified as internal inspection procedures, but are not actively used by the contractors who provide inspection services. These methods are radiography and eddy current.

EMERGING TECHNOLOGIES

In keeping an eye to the future of inspections and how the Agency may assist states and owner/operators in complying with the regulations, preliminary information on emerging methods is also being collected. Such emerging technologies have been developed for use in other applications but are not yet performed on underground storage tanks. A typical source of an emerging technology is the pressurized vessel industry. Examples of such technologies are: acoustic emission, the boroscope, and microwave.

INSTALLATION	UPGRADING	CLOSURE	REMANUFACTURING
Steel / FRP 1. Visual Inspection 2. Pressure Test 3. Internal Tank Diameter (FRP only) 4. Vacuum Test 5. Bubble Test	Steel 1. Tank Cleaning 2. Ultrasonic Test 3. Visual Inspection 4. Holiday Test 5. Dry Film Thickness 6. Barcol Test (optional) 7. Pressure Test 8. Hammer Test 9. Liquid Dye Penetrant 10. Magnetic Particle	Steel / FRP 1. Tank Cleaning 2. Visual Inspection	Steel 1. Tank Cleaning 2. Ultrasonic Test 3. Visual Inspection 4. Pressure Test 5. Liquid Dye Penetrant 6. Magnetic Particle FRP 1. Tank Cleaning 2. Ultrasonic Test 3. Vacuum Test 4. Visual Inspection 5. Holiday Test 6. Dry Film Thickness 7. Barcol Test (optional) 8. Pressure Test 9. Liquid Dye Penetrant 10. Bubble Test

Table 2. Typical Internal Measurement Methods Employed During Inspections

CONCLUSIONS

Available information suggests that no compilation of SOTA internal inspection methods has been prepared to date. The identification and description of these methods in a single document would serve to educate owner/operators in selecting the most appropriate type of inspection under each circumstance (i.e., installation, closure, etc.) during the operational life of the tank. It would provide state regulatory authorities with information necessary to design inspection programs and provide contractors with a variety of UST inspection techniques.

Internal inspections fall into four categories: installation, upgrading, closure, and remanufacture. Several methods have also been identified during the pre-installation phase of the tank's life. However, since the focus of the study is the operational life of the tank, pre-installation methods are not emphasized in this study.

One obvious finding of this study is that, with the exception of visual inspections, the type of inspection performed depends on the status of the tank. For each major activity in the operational life of the tank, there are several different inspection methods which may be applied. Ultimate selection of one method in lieu of another usually depends upon the desired degree of accuracy of the results.

An examination of various applicable standards has revealed that many contain requirements which conflict with those of other standards. In some instances, conflicts between requirements exist within the same standard. For instance, vacuum tests and tank deformation tests are not required by EPA in the preamble to the regulations, but the standards called out in the preamble provide reference to these methods.

Little information is presently available on the impact of tank size on the performance of the test. This is because most methods require that the test be performed a certain number of times within a specified surface area of the tank. The test is then repeated at regularly defined intervals across the entire surface of the tank. Without the benefit of further investigation, this would suggest that tank size has no influence on the performance of the test or its results.

RECOMMENDATIONS FOR FUTURE ACTIVITIES

For the balance of this fiscal year, the scope of this work assignment will focus on the evaluation of the methods identified earlier in our discussion in order to establish a full understanding of their range of applications. Among the specific tasks anticipated are:

- Obtaining data to reveal how or if these inspections are being applied by tank owner/operators as part of a comprehensive maintenance program.
- Investigating the necessity to develop protocol manuals to ensure the standard application of methods by vendors offering internal inspection services.
- Studying the effects of tank size on test results; particularly in the categories of tanks less than 30,000 gallons, tanks ranging from 30,000 to 60,000 gallons, and tanks greater than 60,000 gallons on capacity.

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EVALUATION OF INTERNAL LEAK DETECTION TECHNOLOGY FOR LARGE UNDERGROUND STORAGE TANKS

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ABSTRACT

The performance standard for tank tightness testing established by the EPA regulation requires that the systems used to test underground storage tanks be able to detect leaks as small as 0.1 gallons per hour with a probability of detection of 0.95 and a probability of false alarm of 0.05. This standard was developed to address tanks nominally 37,850 liters (10,000 gallons) in capacity or less, but it also applies to tanks as large as 227,140 liters (60,000 gallons). The accuracy of detecting leaks in large tanks is not well known, and very little experimental data are available to make an assessment. An experimental field study is being conducted to investigate the magnitude of the volume changes that affect the performance of leak detection systems based on tank tightness testing in underground storage tanks with capacities between 75,710 and 227,140 liters (20,000 and 60,000 gallons). The experiments are designed to estimate the magnitude of the volume changes produced by two of the more important sources of noise that need to be compensated for in order to obtain good performance: (1) thermal expansion or contraction of the product in the tank and (2) structural deformation of the tank itself. Models of these physical processes were developed in a previous study on smaller tanks. The data collected in the current experiments will be used to determine whether these models are valid for tanks that are up to ten times larger. In addition, the data obtained from several thermistor arrays deployed in the tank will be used to estimate the magnitude of the horizontal and vertical changes in the temperature of the product in the tank. This paper describes the experiments that will be performed and presents an analysis of the instrumentation.

INTRODUCTION

The United States Environmental Protection Agency (EPA) regulation for underground storage tanks (USTs), published on 23 September 1988, specifies the technical standards and a variety of release detection options for minimizing the environmental impact of tank leakage [1]. With several exceptions, shop-assembled tanks covered by the regulation range in size from several hundred gallons in capacity to very large tanks, with no clearly defined upper limit. Requirements for large, field-erected tanks have not yet been established.

For the tanks currently covered by the regulation, the EPA performance standards for volumetric tank tightness tests require that leaks as small as 380 ml/h (0.10 gal/h) must be detected with a probability of detection (P_D) of at least 0.95 and a probability of false alarm (P_{FA}) of 0.05. Tanks as large as 227,140 L (60,000 gal) are covered by this regulation. Based on the results of an extensive experimental program conducted at the Underground Storage Tank Test Apparatus in Edison, New Jersey, the EPA concluded that achieving this level of performance is within the capabilities of the state of the art for tanks with capacities of approximately 37,850 L (10,000 gal) or less [2]. The EPA developed general design recommendations for tank tightness systems so that this level of performance could be achieved in tests conducted in overfilled and

partially filled tanks of this capacity. The EPA also described the features that are required in order for a tank tightness test to meet its standards. A leak detection system measures flow rate due to a leak, but errors associated with (a) temperature changes in the product inside the tank and (b) structural deformation of the tank itself can interfere with effective detection. The important features, then, are the ones that compensate for these errors. Experiments on a 30,280-L (8,000-gal) tank showed that an array of five or more equally spaced temperature sensors was sufficient to compensate for the thermally induced volume changes providing that adequate waiting periods were adhered to after any addition of product, whether this addition represented a delivery to the tank or whether it constituted topping of the tank (as is required when testing an overfilled tank). The addition of product to the tank produced inhomogeneities in the temperature field that were large enough to prevent an accurate estimate of the mean rate of temperature. This estimate is required for thermal compensation. As a means of minimizing the effect of these thermal inhomogeneities, waiting periods of at least 3 h after topping and 6 h after a delivery were recommended. Any addition also changes the level of product in the tank and, therefore, the pressure that is exerted on the tank walls. This change in pressure causes the tank to deform. The waiting period required to allow the deformation of the tank to subside depends on the properties of the tank and the backfill and native soil surrounding the tank; it could be as much as 12 to 18 h.

Little data are currently available, however, to indicate whether these recommendations are valid for the larger tanks covered by the regulation, and therefore it is unclear whether a tank tightness test that meets the standard established for smaller tanks can achieve the same level of performance when used to test larger tanks. Based upon previous experimental and analytical work, we expect that larger tanks will require (1) more temperature sensors and more accurate estimates of the coefficient of thermal expansion for temperature compensation, (2) longer waiting periods after topping or after a delivery of product to the tank, and (3) an increase in the precision requirements of the temperature and level measurement systems used by the tank tightness test methods. The horizontal and vertical distribution of temperature after topping and after delivery has not been systematically investigated for large tanks; without these data it is not possible to determine the duration of the waiting periods required to let the inhomogeneities in the temperature field decay and to determine the number of temperature sensors needed for compensation. No data exist to describe the temporal characteristics of the volume changes produced by deformation in large tanks. Until such data are gathered, the duration of the waiting period required for these volume changes to become negligible is unknown.

OBJECTIVES

Two sets of experiments will be conducted to investigate the magnitude of the temperature and deformation effects associated with a tank tightness test; one experiment will be conducted in a tank with a capacity of 75,700 L (20,000 gal) and the other in a tank with a capacity of 181,680 L (48,000 gal) or greater. Based on these tests, an assessment will be made of the ability of tank tightness tests to meet the EPA standard when such tests are used on larger tanks. Recommendations for minimizing the errors associated with thermal inhomogeneities and structural deformation will be made, so that the best possible performance can be achieved.

This paper describes the experiments that will be conducted and presents the results of an analysis of the requirements for temperature and level sensors. This analysis gives the precision required of the sensors and the duration of the data collection period in order for a tank tightness test on a 181,680-L (48,000-gal) tank to meet the EPA standard.

MEASUREMENT METHODOLOGY

The temperature and deformation effects were characterized in previous work conducted at the Test Apparatus in tanks of a nominal 30,280-L (8,000-gal) capacity [2]. The current work is thus focused on extending the experimental base to tanks significantly larger than those installed at the Test Apparatus. The previous studies will be used as a baseline against which to compare

the results from the experimental data developed in the current work. The currently planned test program, although more limited in scope than the original study, draws extensively from the instrumentation and experimental designs developed during the course of this previous work.

The current test program requires that both product temperature and level measurements be made for a range of initial conditions in two different-size tanks. A limited range of initial conditions will be generated in each tank, and the tank response then recorded over a period of 6 to 24 hours. Details of specific experimental configurations are discussed in the following sections.

Experiments will be conducted on a 75,710-L and a 181,710-L (a 20,000-gal and a 48,000-gal) UST to estimate the magnitude of the major sources of noise that affect the performance of internal leak detection tests. The experiments will be conducted at operational UST facilities. The experiments are designed so that the impact on operations at the facility being used will be minimal. The sensors will be calibrated prior to any field testing and prepared for immediate implementation at the field-test site. The product temperature changes in the tank will be examined under three conditions: a nearly full tank, an overfilled tank, and a partially filled tank. A special set of experiments will be conducted when the tank is overfilled to determine the deformation characteristics of the tank. Approximately four days of testing will be required for each tank.

The testing program is designed to address the following questions: (1) what are the vertical and horizontal characteristics of the product temperature field, (2) what are the structural deformation characteristics of the tank system, (3) how long does it take for the temperature inhomogeneities due to topping and delivery to subside, and (4) what are the requirements of the temperature and level instrumentation?

Temperature Field. Accurate temperature compensation requires that a sufficient number of thermistors be located in the vertical and that the horizontal differences in temperature be small. The two arrays of thermistors will be used to make an estimate of the vertical and horizontal differences in temperature before, during, and after the addition of product in each of two circumstances, a delivery and topping. Data will be collected: (1) after a delivery that brings the level of product to about 75% of the tank height, (2) after a second delivery that brings the level of product to about 95%, and (3) after the tank has been topped such that the level of product is within the fill tube. At each level of product, the ability of a tank tightness test to compensate for the thermally induced volume changes after the spatial inhomogeneities due to product addition have subsided will be assessed.

Structural Deformation. Structural deformation of the tank occurs in response to any change in the hydrostatic pressure on the tank. Previous studies of this phenomenon suggest that the response of a tank to a step change in pressure (or level) is exponential in form. The details of the shape of the exponential response are largely influenced by the tank material, type of backfill, water table level, and local native soil conditions. Experiments conducted on the EPA tanks in Edison indicate that a relaxation time constant of three hours and an elasticity constant of 100 cm² are not uncommon for the backfill/soil conditions prevalent at the Test Apparatus.

In a nonleaking tank the time constant of the tank can be determined by producing an instantaneous level change in the fill tube of an overfilled tank and monitoring the time history of the volume changes. The time constant of the tank can be determined by fitting an exponential curve to the cumulative volume changes required to maintain a constant level in the tank. An instantaneous level change is produced by inserting a bar of known volume into the tank, after waiting for any previous deformation effects to subside.

Waiting Periods After Topping and Delivery. There are two effects produced by topping and delivery that will affect the performance of a volumetric test method: (1) temperature inhomogeneities and (2) structural deformation. Both effects diminish with time and so can be minimized if there is a mandatory waiting period between filling/topping and testing. The effects of topping and delivery will be determined from the temperature and level data obtained immediately before and after product is added to the tank.

Instrumentation Requirements. In large tanks, the instrumentation noise can be a significant fraction of the total noise. One way to overcome high instrumentation noise is to increase the sampling rate or duration of the test. The requirements of the instrumentation can be determined from an analysis that includes the resolution, the system noise, the duration of the test, and the number of independent samples acquired during a test.

TEMPERATURE AND LEVEL MEASUREMENT SYSTEMS

The systems that will be used to conduct the field experiments consist of two types of measuring devices: temperature and level (height). The temperature measurement system will be used primarily to monitor the product; the product temperature data will be analyzed to estimate the thermally induced volume changes in the tank. Air temperature will also be measured; air temperature data are not central to the experiments or the analysis, however, and will be used only to characterize weather conditions during the experiments.

Two types of product level measurements are required. The first is to measure the height of the product from the bottom of the tank; a pressure sensor with a precision of 5 cm or less will be used. Four sensors will be used to measure the change in product level at each average height. A pressure sensor will be used to measure the level changes when the tank is overfilled into the fill tube, and an electromechanical sensor, an acoustic sensor, or a fiber-optic sensor will be used to measure level changes when the tank is partially filled. The three level sensors that will be used in a partially filled tank are provided by Vista Research. The choice of the primary sensor will depend on the type of experiment being conducted and the availability of access points on the tank. Based upon physical constraints at the test site, efforts will be made to provide data redundancy through multiple independent sensors. The pressure sensor is located at the bottom of one of the thermistor arrays, and is used for all tests. If possible, at least two of the other height sensing devices will be located in and alongside the tubing of the second thermistor array, or will be inserted in the tank through a separate opening.

Under ideal conditions, all of the temperature and level measuring sensors will be deployed in the test tank. In order to achieve this, the tank must have *at least* three access points having diameters equal to or greater than 4 inches. With this arrangement, it should be possible to install the instrumentation and provide unobstructed access for making the required volume displacements. An optimum configuration would place these ports equally along the horizontal axis of the tank. However, because the test tanks will be located at existing commercial installations, it will be necessary to examine the installed configuration prior to testing to ensure that the minimum experimental requirements can be met.

To measure product temperature, two arrays of thermistors will be used. The thermistors, attached to a stainless steel tube, are spaced at intervals of 20 cm (8 in.) along the vertical axis of the tank. To measure air temperature, a single thermistor will be placed in a shaded area outside the tank. Each array, placed in the tank through a fill hole or other appropriate connection, is equipped with a pivoting "arm" that can be lowered to a horizontal position after the array has been positioned. The pivot arm provides for the measurement of horizontal thermal gradients between the tank's centerline and its walls. A tank with an inner diameter of 11.5 ft requires 17 vertically oriented thermistors and a 5.5-ft pivoting arm containing 9 thermistors.

The data quality objective for the instrumentation to be used in the field tests is based upon the EPA performance standard for tank tightness tests [1] and is more fully described in the *Instrumentation Tradeoffs* section of this paper and in [3]. All of the temperature and level measurement systems that have been selected for use in the proposed field tests have the capability to detect of a 380-ml/h (0.1-gal/h) leak with a P_D of 0.95 and a P_{FA} of 0.05 for a given measurement period. The range, resolution, precision, and accuracy of the temperature and level sensors selected for use in the field tests are summarized in Table 1. The minimum duration of the measurement period required for each sensor to meet the data quality objective is presented in the last column of this table. The values presented in Table 1 are based on the following:

- (1) accuracy is defined as the difference between the measured and actual values;
- (2) precision is

defined as one standard deviation of uncertainty in each measurement; (3) the resolution of a sensor is determined from the A/D converter in each instrument and is less than or equal to the required precision for all the sensors except the acoustic sensor.

Table 1. Specifications of the Measurement Instrumentation

Sensor	Range	Resolution	Accuracy	Precision	Duration
<i>Temperature</i>					
Product	5 to 25°C	0.0008°C	0.05°C	0.001°C	1 to 2 h
Air	5 to 25°C	0.0008°C	0.5°C	0.1°C	< 1 min
<i>Product Level</i>					
Absolute Pressure	0 to 3.7 m	0.0012 cm	5.0 cm	5.0 cm	< 1 min
Electromechanical	1 cm	0.00025 cm	n/a	0.00064 cm	2 h
Fiber Optic	1 cm	0.00010 cm	n/a	0.00020 cm	1 h
Acoustic	0 to 2 m	0.00381 cm	n/a	0.00064 cm	8 h

EXPERIMENTS

The conduct of the field tests is constrained by both the experimental requirements and the physical and operational limitations imposed by the tank installation. Since the experiments will be conducted at commercial tank installations (rather than at the UST Test Apparatus), careful attention has been paid to planning the tests during periods of tank inactivity. In general, the test sequences have been organized to maximize the amount of data obtained while simultaneously minimizing the amount of product transfers necessary to establish a particular test condition. During the course of the tests, the tank is filled incrementally from an initial 30% of capacity all the way to overfilled, which is the state of the tank during the final testing at the end of the four-day period. The test sequence is designed to assess the temperature and deformation effects necessary to address the objectives of this study.

The tests will start on a Thursday morning and end on a Monday morning. It is assumed that dispensing operations will occur during the business week between 0800 and 2000 and that no dispensing operations will be conducted over the weekend. The instrumentation will be placed in the tank during normal operations on Thursday to check out the measurement systems and to collect some background temperature data. The tank should be below 50% of its capacity. A delivery of product sufficient to raise the level to about 75% of tank height is scheduled to coincide with the close of tank operations. Temperature and level measurements will be made over the next 12 to 24 h to examine the effects of the delivery. Measurements will terminate when the dispensing operations begin on Friday morning. A second delivery of product, which should nearly fill the tank, is scheduled for the close of business on Friday night. Temperature and level measurements will be made over the next 24 h to examine the effects of this second delivery. On Saturday morning, the tank will be topped, raising the level of the product into the fill tube. The temperature of the added product will be known to differ from that of the product already in the tank. Temperature and level measurements will be made over the next 6 h to study the temperature effects produced by topping. Once the deformation has subsided, which may require an additional 6 to 12 h, a series of experiments will be conducted to estimate the time and elasticity constants that describe the deformation of the tank.

The time constant of the deformation of the tank and backfill/soil system will be determined as follows. A cylindrical bar of known volume will be inserted into the fill tube to produce an instantaneous level change in the product inside the fill tube. The product in the fill tube will be releveled at intervals of 5 to 15 min, and the volume change required to maintain a constant level in the tank will be recorded. This process will continue for 6 to 12 h. On Sunday, the bar will be removed for 6 h and subsequently inserted again for another 6 h. From these level

changes the effective time constant of measurements in the fill tube can be determined. These data can be used to estimate the elasticity constant of the tank/backfill/soil system if the temperature changes in the tank are small. The volume data obtained from measurements made during the releveing will be used to determine the time constant of the tank. The magnitude of the deformation is dependent on the initial level of product, that is, before the bar has been inserted or removed from the tank. Temperature data will be collected to compensate for thermally induced changes during these tests for structural deformation.

INSTRUMENTATION TRADEOFFS

To meet the EPA performance standard for a tank tightness test, the instrumentation used to measure temperature and level measurements in large tanks should not inhibit the detection of a leak of 380 ml/h (0.1 gal/h) and must allow for a P_D of 0.95 and a P_{FA} of 0.05. This requires that the instrumentation noise be sufficiently small that a one-standard-deviation uncertainty in the measurement of the rate of change of volume is less than 115 ml/h (0.03 gal/h). This 115-ml/h estimate assumes that the instrumentation noise is normally distributed with a zero mean and that the signal adds linearly with the noise. For instrumentation noise, the assumption of normality is generally justified. This estimate also assumes that the resolution of the sampled data is smaller than the standard deviation of the noise. Thus, the instrumentation or system noise estimated in terms of volume can be characterized by its standard deviation; the precision of the instrument is defined by the standard deviation of the instrument noise. If the resolution is greater than the inherent precision of the instrument, it is more difficult to characterize the performance of the instrument. To satisfy this data quality objective, the height and temperature sensors must have resolution and precision adequate to sense changes of 115 ml/h (0.03 gal/h).

The sensors, thus, must be able to measure changes to within a one-standard-deviation uncertainty of 115 ml/h. To estimate the resolution and precision of these sensors, it is necessary to specify the *duration* of the test. For tanks less than 37,860 L (10,000 gal) in capacity (for which the EPA performance standard was developed), the duration of a test is usually 1 to 2 h. This is the minimum amount of time required to make a reasonable estimate of the rate of change of volume in the tank from level and temperature measurements. Larger tanks, which are usually only partially filled during testing, may require tests longer than 1 to 2 h, because the sensors required to measure level and temperature changes approach the technological limits of non-laboratory and affordable equipment. At present, most systems that are used to conduct a test on a partially filled tank are automatic tank gauging systems (ATGSs). The duration of tests conducted with ATGSs is typically 4 to 8 h. The precision of the level sensors is typically between 0.00025 and 0.0025 cm (0.00010 and 0.001 in.). For the current set of experiments, the duration of the measurements will be based on the resolution and precision of the sensors being used.

MEASUREMENT OF SMALL LEVEL CHANGES

Tests conducted in half-filled tanks require the highest degree of precision because the height-to-volume ratio is lowest at this product level. A volume-change uncertainty of 115 ml/h in a half-filled 181,710 L (48,000 gal), 3.5-m (11.5-ft) underground tank will result in an uncertainty of 0.000174 cm/h (0.000069 in./h) in the corresponding product-level changes. The sensor precision required to measure a level change of 0.000174 cm/h can be estimated from

$$S_m^2 = n S^2 / (n \Sigma t^2 - (\Sigma t)^2) \quad (1)$$

where S_m = standard deviation of the slope of the least-squares line in cm/h, S = standard deviation or precision of the sensor in cm, n = number of independent points (i.e., degrees of freedom), and t = time in hours.

Eq. (1) describes the one-standard-deviation error in the slope of a least-squares line fit to a number of independent points taken over a period of time in terms of the standard deviation of the ordinate (i.e., sensor precision). Eq. (1) can be used to estimate the minimum duration of the measurement required to obtain the desired S_m , given a sensor with a precision of S . Estimates made with Eq. (1) are valid providing that (1) the standard deviation of the sensor is greater than the resolution, and (2) each sample is independent. The standard deviation represents an estimate of the system noise or precision of the sensor. Eq. (1) can be used to estimate the minimum duration of a measurement made with a sensor whose precision is known, or it can be used to estimate the precision of a sensor given that the duration of the measurement period is specified. In general, the number of independent samples, and therefore the number of degrees of freedom, will be significantly less than the number of points acquired by the sensor, because ambient level and temperature data are highly correlated for periods less than 5 to 15 min.

Table 2 presents the level sensor precision required to obtain a specified S_m for measurement periods of 1, 2, 4, and 8 h. The minimum duration required for sensors with a precision, S , to obtain a S_m of 0.000174 cm/h can be estimated from Table 2 by finding the precision of the sensors in the last column of the table and reading the duration from the first column.

Table 2. Estimate of the Precision, S , of the Sensor Estimated for $S_m = 0.000174$ cm/h for Different Measurement Periods (A level change of 0.000174 cm/h corresponds to a volume change of 115 ml/h in a half-filled, 181,710-L (48,000-gal) tank.)

Duration of Measurement (h)	Number of Independent Points (n)	Standard Deviation of Rate of Change of Sensor (S_m) (cm/h)	Standard Deviation of Sensor (S) (cm)
1	13	0.000174	0.000196
2	25	0.000174	0.000523
4	49	0.000174	0.001435
8	97	0.000174	0.004000

For these calculations, it was assumed that the data were sampled once every 5 min. Thus, it was assumed that there are only 12 degrees of freedom (i.e., 12 independent points) each hour. If a level sensor with a precision of 0.0025 cm (0.001 in.) is used, the one-standard deviation uncertainty in the measured level changes, S_m , is 0.00226 cm/h (0.00089 in./h) for a 1-h test with 12 degrees of freedom; this is equivalent to a volume change of 1,494 ml/h (0.395 gal/h) in a half-filled 181,710-L (48,000-gal) tank. Previous measurements of level and temperature in an underground storage tank suggested that the number of degrees of freedom might be as low as 3 or 4 each hour. As the number of degrees of freedom decreases, the duration of the measurement must increase or more stringent requirements must be placed on the precision of the sensor.

If the resolution of the level sensor is greater than the inherent precision of the measurement system, and the level changes are less than the resolution of the sensor, then the smallest level change that can be measured with a two-point estimate is a resolution cell divided by the measurement period. If the level changes are larger than a resolution cell, however, level changes can be estimated to better than a resolution cell by fitting a least-squares line to the data. The accuracy of estimating the rate of change depends on the number of resolution cells exceeded and the duration of the measurement. A better estimate can be made if we measure the time at which the level is located at intervals of one-half a resolution cell and fit a least-squares line to the data. The number of degrees of freedom is equal to the number of resolution cells minus 1. A more detailed discussion of how to estimate the performance of a system limited by resolution is given in [3].

MEASUREMENT OF SMALL TEMPERATURE CHANGES

We can estimate, for both half-filled and completely filled tanks, the precision requirement of the product temperature measurement system assuming an uncertainty of 115 ml/h in the leak rate, a value of $0.00125/^{\circ}\text{C}$ for the coefficient of thermal expansion, and a 181,710-L (48,000-gal), 3.5-m (11.5-ft) tank. A 115-ml/h volume change corresponds to a standard deviation of 0.0010 and a $0.00055/^{\circ}\text{C/h}$ rate of change of temperature in a half-filled tank and a full tank, respectively. Eq. (1) was used to estimate the thermistor precision required to obtain the specified standard deviation of the rate of change of temperature, S_m , in both a half-filled tank and a completely filled tank as a function of measurement period. This calculation also assumes that the number of independent degrees of freedom was 12 per hour. The results are presented in Tables 3 and 4. The minimum measurement period required to obtain a precision of 0.001°C is less than 1 h for the half-filled tank and approximately 1.5 h for the completely filled tank. If the test duration were 2 h or longer, the precision of the thermistors could be higher than 0.001°C .

Table 3. Precision, S , of the Sensor Estimated for $S_m = 0.0005^{\circ}\text{C/h}$ for Different Measurement Periods in a Half-filled 181,710-L (48,000-gal) Underground Storage Tank

Duration of Measurement (h)	Number of Independent Points (n)	Standard Deviation of Rate of Change of Sensor (S_m) ($^{\circ}\text{C/h}$)	Standard Deviation of Sensor (S) ($^{\circ}\text{C}$)
1	13	0.0010	0.0011
2	25	0.0010	0.0030
4	49	0.0010	0.0084
8	97	0.0010	0.0233

Table 4. Precision, S , of the Sensor Estimated for $S_m = 0.0005^{\circ}\text{C/h}$ for Different Measurement Periods in a Full 181,710-L (48,000-gal) Underground Storage Tank

Duration of Measurement (h)	Number of Independent Points (n)	Standard Deviation of Rate of Change of Sensor (S_m) ($^{\circ}\text{C/h}$)	Standard Deviation of Sensor (S) ($^{\circ}\text{C}$)
1	13	0.0005	0.0006
2	25	0.0005	0.0015
4	49	0.0005	0.0042
8	97	0.0005	0.0116

SUMMARY

Leak detection performance standards currently do not address the impact of increased tank size on the ability of tank tightness tests to satisfactorily meet regulatory requirements. The currently planned experimental program has been devised to expand the understanding of large underground storage tank behavior as it impacts the performance of tank tightness tests. Upon completion of the field tests, the suitability of the currently recommended test protocol features (which were developed during previous evaluations of tank tightness test methods) can be assessed, and, if necessary, modified accordingly.

This paper has presented an analysis of the requirements necessary for temperature and level sensors to detect leaks as small as 380 ml/h (0.1 gal/h) with a P_D of 0.95 and a P_{FA} of 0.05. The analysis shows the tradeoff in test duration as a function of sample interval for independent samples, resolution, and precision.

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SOURCE OF CONTAMINATION ASSOCIATED WITH
CLOSURE OF UNDERGROUND STORAGE TANKS

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ABSTRACT

EPA is currently evaluating several technical and regulatory aspects of underground storage tank (UST) closures. The purpose of this project is to evaluate the effectiveness of various tank cleaning procedures used at closure. A common cleaning procedure, for example, involves removing pumpable residuals with a vacuum truck, manual entry into the tank to scrape residuals off the sides and bottoms (gums and sludge), and then rinsing with water.

During the course of this project, with the help of a tank cleaning company, tank cleaning operations are being observed for several gasoline and diesel USTs. Samples of the original residuals (present before cleaning), the residuals left after cleaning (if any), and aqueous rinseates are being collected and analyzed for both hazardous characteristics (e.g., flash point and corrosivity), chemical composition (including volatile organics, total petroleum hydrocarbons, heavy metals, and oil and grease), and other characteristics (e.g., pH, BOD and TOC of the aqueous phase). Vapor concentrations are also being measured at various stages in the cleaning process. Estimates of residuals volumes are being made both visually and with dipsticks, and in some tanks, phases initially present in the UST are detected with a conductivity probe.

INTRODUCTION

A previous study showed that there are significant amounts of residuals left in underground storage tanks (USTs) at the time closure is initiated. Although 50 to 100 gallons was typical, it was not unusual to find tanks at closure with several hundreds or even thousands of gallons of residual liquids. The handling and removal of these residuals during closure - and the resulting tank cleaning - are being carried out by a wide variety of procedures often dictated more by preferences of local officials or the selected contractor than by objective guidelines. The cleaning procedures typically generate a significant volume of aqueous rinseate that also presents disposal problems.

The earlier review of closure activities for USTs concluded that the tank cleaning methods currently in use appear to be able to satisfactorily clean most gasoline and light oil tanks. This assessment, however, was made only on the basis of interviews and limited observations. No data existed which indicated just how clean tanks do get. Furthermore, the review found that there was no generally accepted method of tank cleaning, nor were there any generally accepted criteria for assessing tank cleanliness. Therefore, it was the purpose of this study to monitor selected tank cleaning methods, to make quantitative measurements of the amounts of residuals left in USTs before and after cleaning, and to characterize the nature of these residuals and any rinseates generated during the cleaning process.

This field monitoring, sampling, and analysis program is currently in progress. Completion of the field activities has been hindered, in part, by the early cold winter in the Boston area where the work is being conducted. Essentially all UST closure activity ceased during the period from November to February. As of mid-February, only three of an anticipated twelve USTs have been sampled during closure. We expect completion of the field activities in March and April, and the preparation of a final report shortly thereafter. As a result, this paper only presents an overview of the field program and the analyses being conducted.

DESCRIPTION OF FIELD PROGRAM

COOPERATION WITH A TANK CLEANING/REMOVAL COMPANY

It was deemed both necessary and desirable to carry out this field program in cooperation with a company that conducted UST cleaning and removals as part of its business. Camp Dresser & McKee (CDM) selected Jet-Line Services, Inc. (Stoughton, MA), a company that offers a range of

environmental and remediation services in the Boston area. Jet-Line was also one of the companies that provided significant background information in the initial survey phase of this program.

The agreement with Jet-Line calls for them to identify UST closures-of-opportunity, i.e., closure jobs they have obtained as part of their normal business that can meet the objectives of the field study (see below). If the UST and proposed cleaning technique are considered to be of interest to the study, and permission is obtained from the site owner/operator, then monitoring and sampling are carried out during the normal course of the closure.

In order to minimize health and safety concerns, and to avoid issues of liability, all measurement and sample collection activities - including those done by a worker inside the UST - are conducted by trained Jet-Line personnel under the general direction of an on-site CDM monitor. Monitoring and sampling activities also follow the requirements of a Quality Assurance Program Plan (QAPP) prepared by CDM.

The agreement with Jet-Line does not require them to modify their cleaning techniques to arbitrarily provide this study with a variety of cleaning methods. It is expected however, that some variations in cleaning methods will occur as a result of site-specific conditions including the nature and amount of residuals found within the tank.

TANK SELECTION GOALS

The goal of this study is to monitor and sample twelve tanks, as follows:

- Five (5) leaded gasoline;
- Five (5) diesel fuel (or No. 2 home heating oil); and
- Two (2) waste oil or other petroleum product.

Furthermore, we hope to have an opportunity to include one or more fiberglass reinforced plastic (FRP) tanks along with the steel tanks that constitute most of the USTs being closed at present.

The final mix of tanks included in the study will necessarily reflect the closures available to Jet-Line within the timeframe imposed on them by CDM.

INFORMATION TO BE COLLECTED

As noted above, the principal objectives of this study are to evaluate the cleaning effectiveness of the closure activities and to generally characterize the residuals found, and generated, during closure. To support these objectives, the following information will be collected for each site included in the study:

- o Estimates of volumes of tank residuals and secondary wastes;
- o Hazardous characteristics and chemical composition of the residuals and secondary wastes;
- o Details of the cleaning method used; and
- o General background information on the UST and the site that may relate to the nature of the residuals found in the UST.

Volume Estimates

During each UST sampling effort, estimates of the volumes of residuals in the UST before and after cleaning (and of secondary waste generated) will be estimated from dip stick measurements, simple volume measurements (e.g., height of waste in 55-gallon drum), pumping rates and durations, or visual estimates. Dip stick measurements in cylindrical tanks can be converted to fluid volumes by standard trigonometric functions.

Where possible, different volume estimates will be obtained for the following:

- o Liquid organic phase: before and after cleaning
- o Aqueous phase: before and after cleaning
- o Rinseate: amount used to clean tank

Hazardous Characteristics and Chemical Composition

Various UST residuals will be sampled and analyzed for both hazardous characteristics (e.g., ignitibility and corrosivity) and chemical composition. Figure 1 outlines the specific analyses expected for samples from various types of USTs.

The analyses specifically include the following:

Characteristics

Ignitibility
Corrosivity
Reactivity
Toxicity Characteristic
Leaching Procedure (TCLP)

Composition

Volatile Organic Analysis (VOA)
Total Petroleum Hydrocarbons (TPH)
Oil and Grease
Biochemical Oxygen Demand (BOD)
Total Organic Carbon (TOC)
pH
RCRA Metals (As, Ba, Cd, Cr, Pb,
Hg, Ag, and Se)
Polychlorinated Biphenyls (PCBs)

In addition, measurements of vapor concentrations inside the UST will be made at various stages in the cleaning/closure procedure.

It is anticipated that modifications to this sampling and analysis program will be made on a case-by-case basis after considering site-specific conditions.

Details on Cleaning Method

The normal cleaning method used by Jet-Line includes the following basic steps:

- 1) Removal of liquids by suction into a vacuum truck (may leave 1 to 2 inches of liquid in tank)
- 2) Manual entry of tank to scrape walls and bottom (material is removed by suction line and/or shovel); and
- 3) Aqueous rinse of the inside of tank (rinseate is removed by suction line)

Details of the actual procedures used at each tank will be recorded. Visual estimates of the cleaning effectiveness will also be recorded.

General Background Information

Where available, the following information will be recorded for each UST sampled:

- o Tank contents (e.g., gasoline, no. 2 fuel oil, waste oil)
- o Tank dimensions, volume, material of construction, and installation details
- o Tank age and condition upon removal
- o Tank depth in ground, and depth to water table

USTs EVALUATED TO DATE

Summary information on the three USTs evaluated to date is provided in Table 1. Analysis of samples collected have not yet been reviewed according to the project QAPP and are thus not presented at this time.

TABLE 1. INFORMATION ON INITIAL USTs EVALUATED

Site No.	RESIDUALS PRESENT BEFORE CLEANING (gal.)			RESIDUALS PRESENT AFTER CLEANING (gal.)		RINSEATE GENERATED (gal.)
	Organic*	Aqueous	Sludge	Organic Liquid	Sludge	
1	4400	17	Trace	1	None	25
2	800	None	1	None	1	None**
3	94	None	70	None	None	50

* All contained No. 2 fuel oil

** Sawdust used instead of water to clean inside of tank

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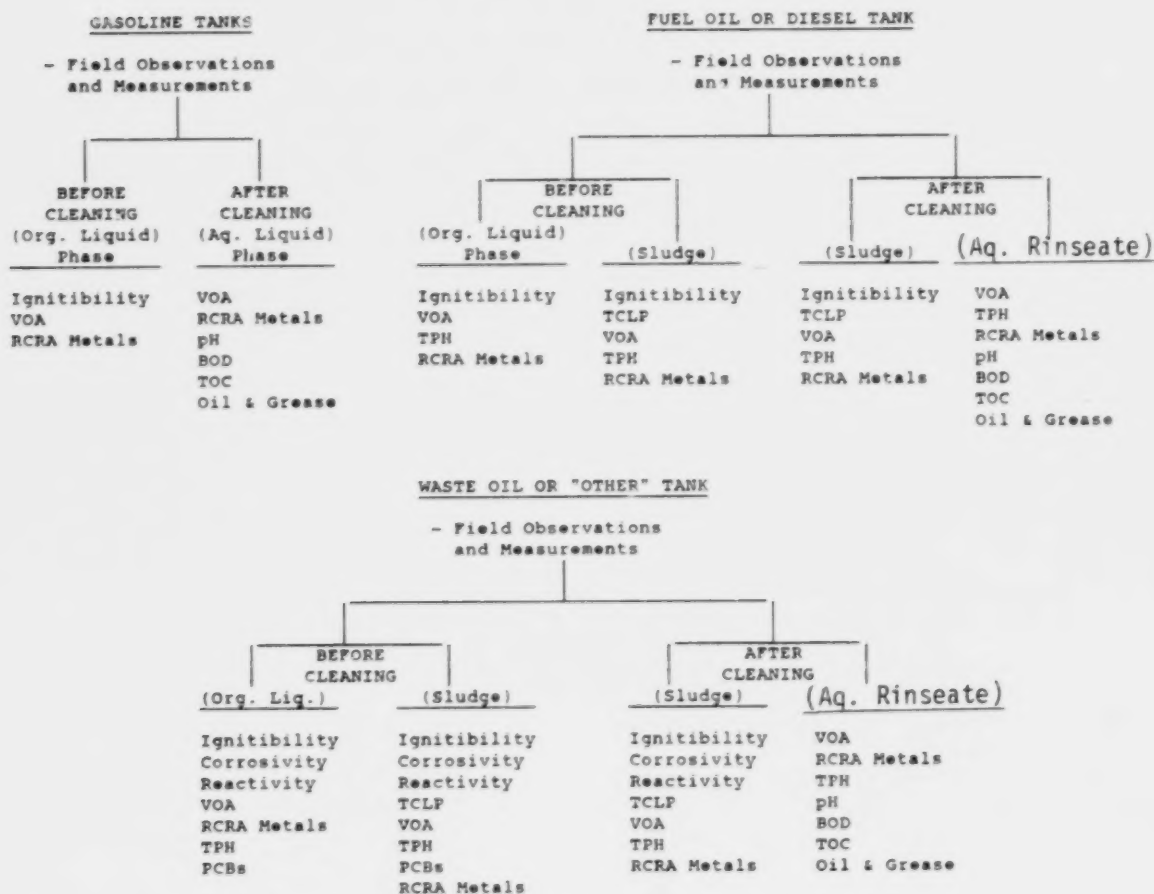


Figure 1. Flow Chart of Samples to be Collected and the Parameters to be Analyzed

REMOVAL OF SOLUBLE TOXIC METALS FROM WATER

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ABSTRACT

The removal of selected, soluble toxic metals from aqueous solutions has been accomplished using a combination of chemical treatment and ultrafiltration. The process has been evaluated at the bench-scale and is undergoing pilot-scale testing. Removal efficiencies in excess of 95-99% have been realized.

The test program at the bench-scale investigated the limitations and established the optimum range of operating parameters for the process, while the tests conducted with the pilot-scale process equipment are providing information on longer-term process efficiencies, effective processing rates, and fouling potential of the membranes. With the typically found average concentrations of the toxic metals in groundwaters at Superfund sites used as the feed solution, the process has decreased levels up to 100-fold or more.

Experiments were also conducted with concentrated solutions to determine their release from silica-based matrices. The solidified wastes were subjected to EP Toxicity test procedures and met the criteria successfully. The final phase of the program involving a field demonstration at a uranium tailings site will be outlined.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administration review policies and approved for presentation and publication.

INTRODUCTION

Conventional treatment to remove contaminants from waste disposal sites or to prevent the spread of contaminant plumes is usually of the brute force mode, where large quantities of contaminated soils are excavated and treated by incineration, solidification, or other related technologies to remove, treat or detoxify the contaminants. In general, these large-scale technologies need to incorporate bulk material handling capabilities to accomplish the desired waste management.

An alternative to such material handling technologies is to remove the metal contaminants from the groundwater, through treatment to extract contaminants, and perhaps recycle the water to the contaminated zone to recover more contaminant adsorbed to the soils in contact with the groundwater. The technology proposed is a combination of chemical treatment and ultrafiltration to enhance the recovery of toxic metals from the water. The technology has been evaluated at the bench-scale level for the removal of radioactive cations from waste water streams (1,2). The technology appears suitable for the removal of toxic metal cations from contaminated groundwater surrounding industrial waste disposal sites and for the treatment of industrial effluents.

In the past year, chemical treatment in combination with ultrafiltration has been evaluated through funds allocated by the Emerging Technology Program of the United States Environmental Protection Agency (USEPA). The Emerging Technology Program, part of the Superfund Innovative Technology Evaluation (SITE), provides guidance and funding for new technologies which may become tools in the cleanup of environmental pollution. The two-year evaluation of the combined chemical treatment and ultrafiltration technique began by conducting experiments in laboratory-scale equipment, to verify the process capabilities for the removal of hazardous toxic metals which may be present in groundwater or industrial wastes.

Thus far, only four metals have been evaluated with the process. They are cadmium, lead, mercury, and arsenic; indicative of metals present in groundwater associated with hazardous waste disposal sites. The program to establish the viability of the process has progressed smoothly, results achieved from the program will be discussed, and proposed efforts to conclude the second year of the contract, which takes the technology through pilot-scale testing and field trials, are outlined.

TECHNOLOGY DESCRIPTION

The emerging technology reported here evolved through efforts by Atomic Energy of Canada Limited (AECL) to remove dilute concentrations of radioactive species from waste waters.

The process involves contacting the waste water with water-soluble macromolecular compounds added to the waste solution to form complexes with the soluble heavy metal ions. A high molecular weight polymer, generally a commercially available polyelectrolyte, is added to the waste solution to form the selective complexes. The polyelectrolyte quantities needed to achieve the separation of metal ions are generally in the parts-per-million range.

The solution is then processed through an ultrafiltration membrane system which retains the macromolecular complexes (retentate), while allowing uncomplexed ions such as Na^+ , K^+ , Ca^{++} , Cl^- , SO_4^{--} , NO_3^- , etc., to pass through the membrane with the filtered water (permeate). The filtered water can be recycled, or discharged depending upon the removal efficiency desired. A removal efficiency approaching 100% can be achieved for metal ions which have been complexed.

The technology as described can be applied to separate toxic heavy metal ions such as Cd, Cr, Hg, Ni, Cu, Zn, As and Pb from leachates generated in Superfund sites (3). Other inorganic and organic materials, if present as suspended and colloidal solids, can also be removed. The ultrafiltration membrane can be chosen with a sharp molecular weight cut-off, to further enhance separation. The toxic metals can be concentrated in a small residual volume which should be amenable to conventional solidification treatment.

BENCH-SCALE TESTS

Separation Studies

The first year of the test program was divided into five tasks: first, to evaluate the major variables using a factorial design having five variables, each at two levels, with fixed levels of metal contaminants; second, to study the extent of fouling and the cleaning techniques needed to recover the flux rate of the membranes; third, to evaluate the system response to changes in toxic metal concentrations; fourth, to perform a second evaluation of fouling and the cleaning techniques necessary to operate a continuous system; and fifth, to conduct a series of tests at three levels for each dominant variable, to optimize the technique for the removal of toxic metals.

The bench-scale tests were performed using Amicon ultrafiltration stirred cells. Cells with volume capacity of 50 mL or 200 mL, and equipped with rated membranes having molecular weight cut-off of 10 000, were used. The metal ions were complexed with polyelectrolytes, i.e., polyethylenimine, with a molecular weight of 50 000 and Gantrez AN 119, a polymethyl vinyl ether/maleic anhydride copolymer, of similar molecular weight. The operating conditions for the test series are summarized in Table 1.

TABLE 1. BENCH-SCALE EXPERIMENTAL CONDITIONS

Variable	Test Conditions	
Solution pH	alkaline	acidic
Membrane Type	polysulfone	cellulose acetate
Polyelectrolyte	polyethylenimine	Gantrez
Polyelectrolyte	10 times the	
Concentration, mg/kg	metal concentration	0
Toluene, mg/kg	1000	0

Cadmium removal efficiencies indicate that: the separation technique is more effective at elevated pH values; removal efficiency of about 99% can be obtained; and, it was difficult to distinguish the minor effects of other operating parameters such as membrane type, polyelectrolyte type and the presence of organics (toluene) on the removal efficiencies.

Removal efficiencies of 90% or higher were obtained for mercury. In contrast with cadmium, the removal of mercury is less affected by solution pH. Polyethylenimine appears to be a better complexing agent than Gantrez. Factors such as membrane type and toluene had no apparent effect.

Lead is a special case, because its starting concentration in the feed solution was two orders of magnitude higher than the other heavy metal ions examined in this study. Like cadmium, it is more effectively removed from solution at elevated pH values. However, the removal efficiencies are equally good when no polyelectrolyte was added to the feed solution, an indication that most lead is removed by precipitation as hydroxide.

Relatively poor separation efficiencies of <35% for arsenic were achieved with and without the addition of either polyelectrolyte. The reason is that a major fraction of arsenic is present in solution as an anionic species, i.e., AsO_4^{3-} , while most other metal ions are in the form of cations. The results obtained for arsenic indicate the present limitation of the proposed complexing polymers in the chemical treatment and ultrafiltration technique.

Polysulfone membranes experienced severe fouling, with permeation rates declining more than 70% when solutions containing polyethylenimine were treated. Gantrez caused less fouling to the polysulfone membranes, but the permeation reduction was also quite severe at high Gantrez concentrations.

Cellulose acetate membranes, in contrast, are essentially free from fouling caused by either electrolyte; only some slight fouling with permeation rate reductions of about 20-40% was experienced when either polyelectrolyte was used at a relatively high concentration in the lead test series. However, even with the limited fouling observed, the permeation rate of the cellulose acetate membranes is still five to ten times lower than achieved with the fouled polysulphone membranes.

Operating parameters such as pH and the presence/absence of toluene did not appear to have any impact on the fouling behaviours of the ultrafiltration membranes in these bench-scale tests.

Since the polysulfone membranes showed significant fouling in the first series of tests performed, only this type of membrane was used in a number of repeated tests to produce similarly fouled membranes, to evaluate the effectiveness of different chemical cleaning solutions. Four chemical cleaning solutions were compared: Tergazyme detergent; sodium hydroxide and hydrogen peroxide; methanol acidified with hydrochloric acid; and, deionized water as the control cleaning solution.

In each test, a membrane was subjected to a pure-water test to obtain the initial permeation rate. Ultrafiltration of the test solution containing

metal polymer complexes followed, to obtain a water recovery of 90%. Then, the following steps were taken: rinsing with deionized water, cleaning with one of the chemical solutions, and, finally, re-rinsing with deionized water. At the end, a pure-water test established the post-test permeation rate.

The results indicate:

For a polysulfone membrane fouled by polyethylenimine, acidified methanol is the best cleaning solution to restore the permeation rate. Tergazyme detergent caused further severe fouling to the polysulfone membrane which had already been fouled by polyethylenimine. The detergent may contain an anionic surfactant which reacts with the cationic polyelectrolyte, to form an insoluble product which plugs the membrane pores. Sodium hydroxide-hydrogen peroxide did not remove the foulant better than deionized water.

For a polysulfone membrane fouled by Gantrez, cleaning with deionized water was able to restore most of the permeation rate. Overall, it is easier to remove this polyelectrolyte than polyethylenimine from the fouled polysulfone membrane. Acidified methanol was less effective, while the other two cleaning solutions are slightly more effective than deionized water.

The repeated tests performed for the membrane cleaning tests provided an opportunity to check the reproducibility of the performance of the chemical treatment ultrafiltration combination technique. The results indicated that relatively consistent results such as separation efficiencies, permeation rates and permeation reduction can be reproduced for tests carried out under the same operating conditions with different membranes.

The performance of this separation technique may be affected by the variability of the feed concentrations of the metal ions. Varying the dissolved metal concentration in a feed solution represents a realistic situation where the separation process is applied using a predetermined set of operating conditions. Metal separation efficiencies, membrane fouling behaviour and the effect of chemical cleaning were studied. Polysulfone membranes were chosen to allow the study of membrane fouling and cleaning. An alkaline solution pH value was selected to get high removal efficiencies for the heavy metals. No toluene was added to the feed solution, since the earlier tests did not indicate any adverse effects of separation when toluene was present or absent.

The test program produced optimum conditions for the dominant variables and provided additional verification of the process to remove soluble metal cations from solution. The addition of excessive amounts of polyelectrolyte did not enhance the separation observed from the first series of experiments. Variation of the pH values improved the separation, but again, at increasing alkalinity levels, the improvement in the separations observed were minimal. Finally, further evaluation of the polyelectrolyte selection did not produce large enough differences to dominate the selection for the pilot-scale tests.

Solidification and EP Toxicity Tests

Next, a solidification study was performed on some of the concentrated waste products generated from several of the above tasks, specifically to

establish the success in producing a quality product which will be strong enough to survive the structural integrity procedure in the EP Toxicity procedure, and provide concentrations of the contaminants below the limits set out in Table 1 of 40 CFR 261.24 (4). Whether the concentrated waste had a harmful effect on the matrix stability or its ability to retain heavy metals had to be resolved.

There were three matrices chosen, all cementitious-based to immobilize the concentrated product which will arise from the volume reduction of the waste solutions treated by the ultrafiltration membranes. The three matrices were: ordinary Portland Cement, Type I (OPC); Aquaset, a proprietary product of Fluid Tech, Inc.; and a mixture of OPC and blast furnace slag. Products were prepared with ten- and twenty-fold increases in metal and polyelectrolyte concentrations, typically expected from recycle of the waste solutions through an ultrafiltration system. The samples were molded and then cured for periods of seven days. The samples were released from their molds, each in turn placed in a compaction tester to establish the structural integrity of the specimen, and then subjected to the EP Toxicity test procedures (4).

Results are available at this time for only the OPC specimens. All formulated specimens successfully passed the structural stability test, allowing the specimens to be leached intact. The test matrix included both electrolytes and metal concentrations at ten and twenty times the average feed concentration. The measurement of metal content of the leachates indicated the levels were less than the detection limits available for the analytical instruments used, and well below the maximum concentration of contaminants for characteristic of EP toxicity listed 40 CFR 261.24 (4).

PILOT-SCALE TESTS

A schematic of the pilot-scale test facility is presented in Figure 1. The ultrafiltration membranes used were purchased from the Romicon and Amicon corporations. The modules (or cartridges) are constructed with hollow fibre membranes, and made with polysulphone. The Amicon module has twice the surface area of the Romicon unit.

A hollow fibre configuration for the ultrafiltration membrane system was selected because of its many attractive features (5). These include: high surface area-to-volume ratio; low holdup volume; low energy consumption; and relatively easy cleaning by "backflushing". Minor disadvantages include higher membrane replacement costs and susceptibility to plugging.

The choice of polysulphone material for the membrane was based on the high flows capable with this material, compared to that of cellulose acetate, in spite of the increased fouling of the polysulphone membranes observed in the first test phase. Other reasons for the choice were the operating range established from the first series of tests, which indicated alkaline conditions were better, and to overcome the distinct possibility of poor lifetimes expected of cellulose acetate at elevated pH levels.

The pilot-scale test program was established to obtain engineering design data to permit the building of the field test unit, and to permit some initial cost evaluations to be undertaken. Tests were of three general types to evaluate the operation of single membrane modules: first, in a batch mode, by continuous recycle of both permeate and retentate streams to the feed tank, to establish the separation efficiency; second, in a concentration mode, enriching the feed by allowing the permeate to be discharged from the system while recycling the retentate to the feed tank; and third, in a feed and bleed mode, where fresh feed is introduced to the system while simultaneously removing concentrate and permeate, with the bleed-to-permeate ratio fixed by the specified recovery.

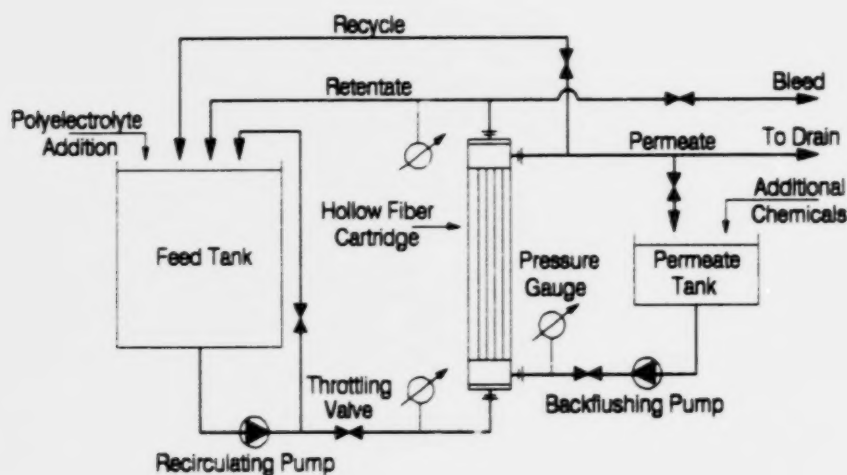


Figure 1. Schematic of pilot-scale unit

The operating conditions for the three types of pilot-scale tests are given in Table 2. Most experiments covering batch and concentration modes of operation are complete. The majority of analytical results for the separation efficiencies of the heavy metals are pending. Preliminary analysis of some analytical results for batch-mode tests have revealed removal efficiencies in the range of 85-99% for lead, mercury and cadmium from a combined alkaline feed stream. The analysis of organic content of the permeate water indicated that most, if not all, of the polyelectrolyte is being removed from the feed stream by the membranes. The feed flow rate was 4000 US gal/day and permeate flux varied from 30 to 75 US gal/ft² day. Unlike the bench-scale test results, the initial pilot-scale data showed appreciable loss of metals. It appears the loss is due to adhesion, adsorption, and free settling of metal complexes and precipitates within the process equipment. Methods to account for and minimize losses, and to recover the metals, are being studied.

TABLE 2. PILOT-SCALE EXPERIMENTAL CONDITIONS

Variable	High Value	Low Value
Solution pH	alkaline	neutral
Membrane Surface Area (ft ²)	30	15
Operating Pressure (psig)	45	25
Feed Rate (US gal/day)	6500	4000
Polyelectrolyte	10 times the	0
Concentration (ppm)	metal concentration	
Metal Concentration	10 times	0.5, 0.3, 60
in feed (ppm)	the low value	
[cadmium, mercury and lead]		

The hydraulic behaviour of the new membranes after a few days of usage produced a steep drop in the permeation rate of about 30%, mainly due to compaction of the membranes. After this initial irreversible decrease, the permeate rate decreased more slowly, eventually reaching a point where back-flushing or chemical cleaning was necessary to recover the flux to reasonable levels. Once removal of the polyelectrolyte begins, additional permeate flux loss is evident (see Figure 2). The loss becomes more dramatic when alkaline feed solution containing lead is concentrated. A permeate flux loss of up to 75% from membrane compaction, physical ageing by extended operation, and by plugging of pores by particles, was not uncommon in the pilot-scale tests. These flow results confirm the initial bench-scale studies performed with flat membranes.

DEMONSTRATION TESTS

The demonstration tests are expected to take place at a site near the town of Elliot Lake, Ontario, about 400 km from the Chalk River Nuclear Laboratories site. A substantial quantity of uranium mine tailings was deposited within the property boundaries during operation of the Nordic Mine by Rio Algom Limited from 1957 to 1968. The waste, while mildly contaminated with residual quantities of uranium, radium and thorium, also contains other metal ions including iron, calcium, magnesium, aluminum, copper, cobalt, zinc, lead, nickel, chromium and cadmium. The tailings impoundment has been investigated to determine the migration of acidic groundwater seepage. While the contaminated groundwater does not constitute a hazard because of its remote location and limited migration of the heavy metals and radioactive ions (6), it provides an opportunity to field test the developing technology.

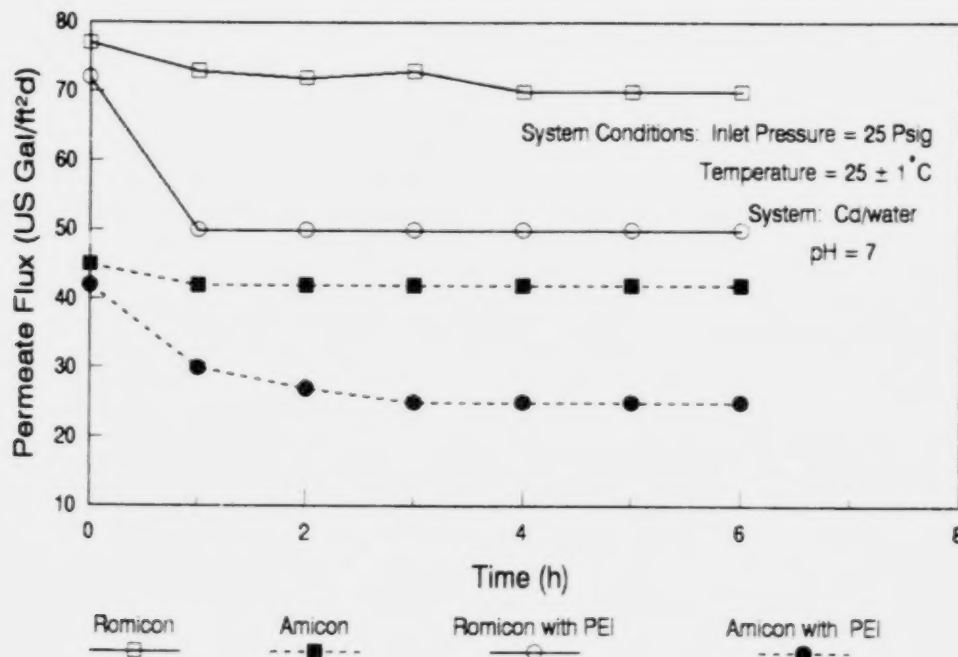


Figure 2. Permeation rates of hollow fibre modules

The project involves building a mobile facility capable of treating about 30 L/min of contaminated groundwater. After commissioning the mobile unit, it would be transported to and operated at the tailings impoundment. The technology will be assessed to determine its potential to decontaminate a plume of toxic metal ions released in the groundwater from the tailings impoundment.

CONCLUSIONS

Based on the tests performed thus far, we can state:

- Among the four heavy metals examined, cadmium, lead and mercury are effectively removed (99%), while arsenic removal was less effective.
- Separation of heavy metal ions is better in an alkaline medium than in an acidic medium and membrane composition is not a major factor.
- The presence of toluene in feed water does not seem to affect the metal separation efficiency nor the membrane fouling rate, although its effect on membrane integrity during extended operation must not be ignored.
- Initial data from the pilot-scale studies have confirmed high separations are achievable and design data are available for the field test facility.

In summary, the proposed technology could be applied to remove selectively toxic metal ions from the Superfund site leachates. The residual volume produced in this technique is significantly smaller than volumes

achieved in other conventional water treatment techniques, such as evaporation, ion exchange and reverse osmosis, where large quantities of non-toxic ions are also included in the concentrated products. Significant savings may be realized due to the reduction in the final volume of the stabilized product that needs to be disposed of. Even though it is not a stand-alone treatment process, this chemical/ultrafiltration combination method may contribute to a cost-effective scheme which integrates a number of separation processes to provide treatment for complex waste streams. The proposed technology may be utilized to provide in-situ cleanup of contaminated soils, by extracting the contaminants from the groundwater, and by recycling the water to the contaminated zone to recover more contaminant adsorbed to the soils.

ACKNOWLEDGEMENT

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Laboratory Studies of the Thermal Destruction
of Toxic Organics in Sewage Sludge

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ABSTRACT

Limited field data are available concerning organic emissions from sewage sludge incinerators. This is of particular concern because hydrophobic hazardous organic compounds, such as certain pesticides, polynuclear aromatic hydrocarbons, and polychlorinated biphenyls, have been shown to partition onto the sludge during the wastewater treatment process.

Laboratory thermal decomposition studies were undertaken to evaluate potential organic emissions from sewage sludge incinerators. Precisely controlled thermal decomposition experiments were conducted on sludge spiked with hazardous organic compounds, on mixtures of pure compounds in absence of sludge, and on unspiked sludge.

The following trends were observed:

- The sludge exerted little if any effect on the destruction of very fragile contaminants.
- If a contaminant was intermediate in thermal stability, it was more difficult to destroy in the presence of the sludge.
- If a contaminant was very stable in the pure mixture, the sludge enhanced its ease of destruction.
- Fluidized bed systems appeared superior to multiple hearth for control of organic emissions.
- The majority of the observed decomposition products were from the biomass decomposition, not the spiked contaminants.

While incineration has been used to dispose of sewage sludge since the 1930's, concern regarding potential environmental insult due to organic emissions from this disposal method has developed only recently (1-5). Very little is known about the fate of hazardous organic constituents or even about total mass emissions of organic material from sewage sludge incineration. The data that do exist (6-10) suggest that some compounds

emitted from sludge incinerators may present a human health hazard, and the mechanism of their formation warrants further study.

EXPERIMENTAL

To study the thermal decomposition of common sewage sludge contaminants, and to identify products of incomplete combustion (PICs) from contaminated sewage sludge, thermal decomposition studies were conducted on two high temperature flow reactor systems, the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) System and the Thermal Decomposition Analytical System (TDAS) (11,12). Both of these systems incorporate a precisely controlled fused silica tubular reactor and in-line gas chromatograph (TDU-GC) or gas chromatograph/mass spectrometer (TDAS). The systems may be operated in a pyrolysis or oxidation mode, at temperatures between 300°C and 1100°C, and reaction times of 0.25-6.0 s.

Thermal decomposition studies were conducted on a relatively clean sludge spiked with contaminants, on mixtures of pure contaminants (without sludge), and on unspiked sludge. The contaminants which were studied were heptachlor, pentachlorophenol, diphenylnitrosamine, pyrene, butylbenzyl phthalate, 2,3',4,4',5-pentachlorobiphenyl, azobenzene, and technical-grade nonylphenol. The sludge was spiked at about 1 mg/g with the organic components, except nonylphenol, which was spiked at 10 mg/g. These levels are at least an order of magnitude greater than those typically found in "real world" sludges, but such spike levels were required to minimize interferences from the sludge matrix. Reactor temperatures for both systems were varied over the range of 300°C-1000°C, and a 2-second gas-phase, mean, residence time ($\bar{t}_r$) at temperature was maintained for all experiments.

A few experiments were performed to simulate the effect of the upper hearths (drying zone) of multiple hearth incinerators on the destruction of spiked sludges. The behavior in this zone was mimicked by gradually heating the sludge in the insertion region of the TDU-GC while maintaining the reactor at a low temperature. Thus, a single sludge sample was placed in the sample insertion region of the TDU-GC, and was successively heated at 15°C/min in nitrogen over four temperature ranges. These temperature ranges were 50°C to 200°C, 200°C to 300°C, 300°C to 400°C, and 400°C to 500°C. The gas-phase residence time of desorbed species in the insertion region was less than one second. During each of the four sets of experiments, the reactor was maintained at a nondegradative temperature (300°C). While the sample was being heated over a given temperature range, any evolved species were condensed at the head of the in-line gas chromatographic column. After these species were collected, they were analyzed via GC/FID.

RESULTS

The results of thermal oxidation and pyrolysis of the mixture and the spiked sludge along with that of the other test are summarized in Table 1 by the temperature for 99% destruction at $\bar{t}_r = 2.0$ s ($T_{99}(2)$) in order of increasing stability under pyrolytic conditions. Diphenylnitrosamine was

TABLE I
T₉₉(2) (°C) OF TEST COMPOUNDS

Compound	Pyrolysis			Oxidation		
	Mixture	Sludge	Δ	Mixture	Sludge	Δ
Heptachlor	450	460	+10	490	490	0
Butylbenzyl Phthalate	500	500	0	400	480	+80
Nonylphenol	570	610	+40	480	510	+30
Azobenzene	600	640	+40	600	620	+20
Pentachlorophenol	690	870	+80	640	730	+70
Diphenylamine	780	840	+60	620	670	+50
2,3',4,4',5-						
Pentachlorobiphenyl	870	820	-50	760	740	-20
Pyrene	1000	>1000	--	720	680	-40

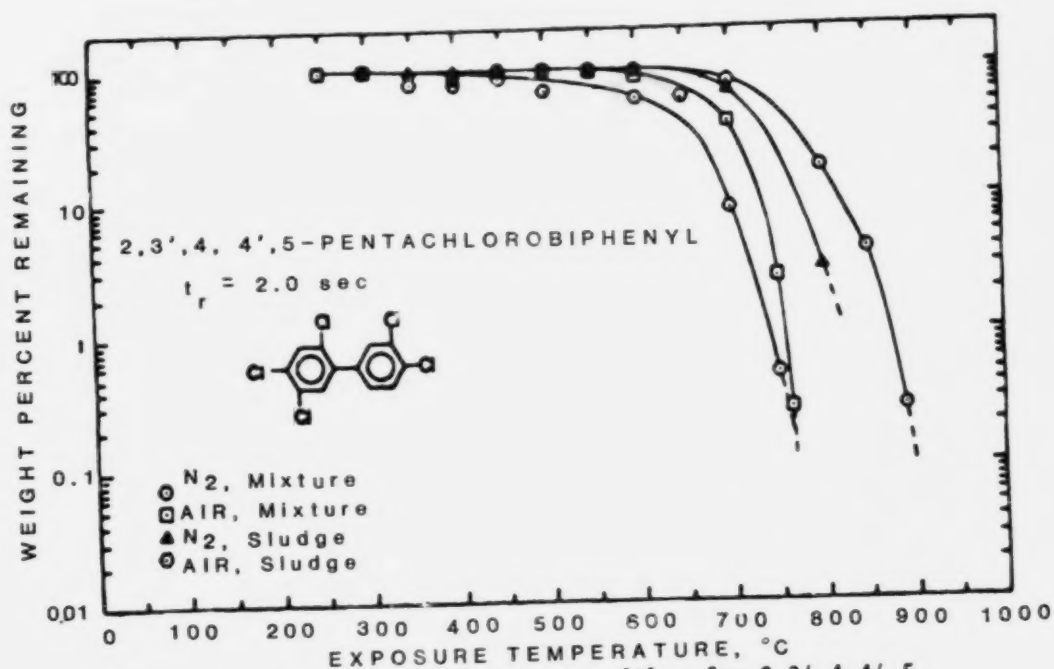


Figure 1. Thermal decomposition profiles for 2,3',4,4',5-pentachlorobiphenyl.

converted to diphenylamine at transport temperatures ($<275^{\circ}\text{C}$); consequently, our thermal stability data are for the product, diphenylamine.

Inspection of Table 1 shows that the test materials are generally more stable under pyrolysis than oxidation for a given matrix (i.e., spiked onto sludge versus run in a mixture of pure compounds). This result is not surprising in light of numerous other combustion and pyrolysis studies in the literature, and can generally be accurately interpreted using chemical reaction kinetic theory (13,14). However, there is a more interesting observation concealed in the data. There is a general trend of increasing stabilization of the test compounds by the sludge matrix as the $T_{90}(2)$ of the compound increases. This holds true except for the two most stable compounds 2,3',4,4',5-pentachlorobiphenyl (PCB) and pyrene, which exhibit destabilization by the sludge (cf. Figure 1).

A multitude of PICs were observed to form from the thermal degradation of the mixture, the unspiked sludge, and the spiked sludge. From these three sets of experiments it was clear that some of the PICs formed from the thermal degradation of the spiked sludge were formed from degradation of specific contaminants, others were formed from degradation of the sludge biomass, while others had to be attributed to interactions of the biomass and the contaminants. These data are summarized in Table 2 along with a statement of the possible source of the observed PICs.

The source of the PICs was assigned based on 4 factors: 1) relative yields from the mixture and sludge, 2) temperatures of maximum yield compared to temperature for decomposition of possible precursors, 3) general principles of reaction kinetics, and 4) the large precursor concentration for the sludge and nonylphenol. Some precursors for some PICs could be specifically identified, while other PICs could occur as decomposition products of several components of the contaminant mixture or the sludge.

DISCUSSION

The decomposition of heptachlor and butylbenzyl phthalate are expected to be dominated by fast unimolecular reactions (15). In the case of heptachlor, a concerted elimination of HCl is expected to be the dominant destructive pathway although simple carbon-chlorine bond rupture may contribute. The rate of this reaction is independent of reaction atmosphere and thus no (or a very small) change in stability due to the presence of sludge is observed. In a similar manner, the decomposition of butylbenzyl phthalate is expected to have a large contribution from the concerted reaction to form 1-butene and the corresponding acid. This is observed in pyrolysis; however, the oxidation data are not conclusive. The thermal oxidation profile has an inflection which indicates the presence of a co-eluting impurity that may cause the butylbenzyl phthalate to appear erroneously more stable when spiked into the sludge.

The four contaminants of intermediate stability (nonylphenol, azobenzene, pentachlorophenol, and diphenyl amine) are expected to be

Table 2
Summary of Thermal Decomposition Products

Product	Pyrolysis			Oxidation			Possible Major Source
	Mixture	Sludge	Spiked Sludge	Mixture	Sludge	Spiked Sludge	
Cyclopentadiene			800				Sludge
C ₅ H ₈	600						Nonylphenol
Benzene	1000	800	900		850	850	Sludge
Hexatriene			700				Sludge
Cyclohexadiene	750		700				Nonylphenol
C ₆ H ₈	800						Nonylphenol
C ₆ H ₁₀	800			500			Nonylphenol
C ₇ H ₈	700						Nonylphenol
Toluene	800	800	800	500	850	850	Sludge
Dichloroacetylene				850			PCP, PCB or Heptachlor
2H-Pyran-2-one						850	Nonylphenol or Sludge
C ₇ H ₁₄			800				Nonylphenol
Chlorocyclopentadiene			800	500			Heptachlor/Sludge
Dimethyltetrahydrofuran						475	Nonylphenol or Sludge
Phenylacetylene	750		850				Nonylphenol
Benzonitrile	1000		800			850	Diphenylamine or azobenzene/sludge
Styrene	750	850	800		850	850	Sludge
Xylene/Ethylbenzene	700	850	850		850	800	Sludge
Benzaldehyde	800	800	750	700	850	800	Sludge
Methylbenzaldehyde						850	Sludge
Quinone						825	Sludge
C ₈ H ₁₀			800				Nonylphenol
Benzofuran	650		750	475			Mixture or Sludge
Dihydrobenzofuran	700		700				Nonylphenol
C ₃ -Benzene	700		700				Nonylphenol
C ₈ H ₁₂	600						Nonylphenol
1H-Indene	700		750				Nonylphenol
C ₉ H ₁₀	625			475			Nonylphenol
Naphthalene	800	800	800				Mixture or sludge
Indenone						850	Nonylphenol or Sludge
Methyl-1H-Indene	700		850				Nonylphenol or Sludge
Methylbenzofuran	700		700	475		850	Mixture
Phenol	700		850	475		800	Nonylphenol or Sludge
Methylphenol/Benzyl alcohol	800		700				Nonylphenol
C ₃ -Alkenylphenol	625		700	475		475	Nonylphenol
C ₄ -Alkenylphenol	625		850	475		475	Nonylphenol
C ₅ -Alkenylphenol	625		850	475		475	Nonylphenol
C ₆ -Alkenylphenol	850		850				Nonylphenol
C ₇ -Alkenylphenol	825		850				Nonylphenol
C ₄ -Alkenyl-aryl-phenol						475	Nonylphenol or Sludge
Naphthalenol	850		700	475			Mixture
Phthalic Anhydride	825		850	800			Butylbenzylphthalate
Acenaphthylene/Biphenylene	1000					800	Mixture
Acenaphthylene/Biphenyl	1000						Mixture
Diphenylamine	800		850	400		800	Diphenylamine
9H-Fluorene			850				Sludge
9H-Carbazole	800		800	800		850	Diphenylamine/sludge
Dibenzofuran			850				Mixture or Sludge
C ₆ -Alkadienylbenzene	700		700				Nonylphenol
C ₇ -Alkadienylbenzene	700		700				Nonylphenol
Tetrachloropropyne				850			PCP, PCB or Heptachlor
Anthracene/Phenanthrene			850				Sludge
Trichlorobenzene			800				PCB
Tetrachlorobenzene	800		800				PCB
Pentachlorobenzene	800						PCB
Trichloronaphthalene	800						PCB
Tetrachloronaphthalene	800						PCB
Pentachloronaphthalene	800			400			PCP, PCB or Heptachlor
Trichlorodihydronaphthalene				800		800	Heptachlor or PCP
Hexachlorodihydronaphthalene	800						PCP or Heptachlor
Tetrachlorofuran				800		800	Heptachlor or PCP
Biphenylcarbonitrile				850			Diphenylamine
Hexachloromethanocyclohexene	500						PCP or Heptachlor

1 Approximate temperature of maximum yield (°C)

2 Underline denotes major product. Relative yields cannot be compared between matrices.

3 Multiple sources are possible

4 / denotes interaction between components to produce observed product

destroyed by bimolecular pathways. Abstraction of H by OH or O is expected to dominate under oxidative conditions. Displacement of the aromatic substituents from the contaminants by H is expected to dominate under pyrolytic conditions. The stabilizing effect of the sludge suggests that it is a radical scavenger which lowers the reactive radical concentration and slows the rate of destruction.

Known scavengers such as benzyl ($C_6H_5CH_2$) and allyl (C_3H_5) may be readily produced from the degradation of the sludge biomass (16). These radicals are resonantly stabilized and may therefore exist long enough to efficiently scavenge H atoms to form toluene and propene. Scavenging of H atoms under oxidative conditions also reduces O and OH concentration by reducing the rate of the chain branching reaction $H + O_2 \rightarrow O + OH$ (17).

However, one must still rationalize the destabilizing effect of the sludge on the two most stable contaminants, 2,3',4,4',5-pentachlorobiphenyl and pyrene. Both compounds are again expected to decompose by H abstraction by O or OH under oxidative conditions. Under pyrolytic conditions 2,3',4,4',5-pentachlorobiphenyl is expected to decompose by Cl displacement by H while pyrene probably decomposes by H abstraction. In either case, an increase in radical concentration is required to explain the destabilizing effect of the sludge. We have hypothesized that the higher temperature required for destruction of these species (>700°C in air and >800°C in nitrogen) is sufficient to destroy the benzyl and allyl radicals to levels such that they are not effective scavengers. Instead, the decomposition of the sludge provides a large increase in the concentration of reactive radicals and an increased rate of destruction of the stable contaminants.

Of the 63 PICs reported in Table 2, we estimate that 41 originated primarily from decomposition of the contaminants, 10 originated solely from the sludge, 9 could have contributions from the sludge and the contaminants, while only 3 could be clearly attributed to sludge/contaminant interaction. The majority of the observed PICs were chlorinated and non-chlorinated aromatic species while most of the remainder were chlorinated and non-chlorinated short-chained unsaturated aliphatic hydrocarbons. Many of the observed non-chlorinated aliphatic species could be attributed to nonylphenol side chain decomposition products. There was very little evidence of increased chlorination (the chlorine source being the contaminants) of hydrocarbon species (primarily from sludge biomass degradation). This is as expected based on the large H/Cl ratio in the system due to the excess of sludge and the generally unfavorable nature of displacement of H by Cl (18). In fact, numerous chlorinated species which were observed from the degradation of the mixture were not observed from the spiked sludge. The H atoms from the sludge facilitate Cl displacement and lower the concentrations of chlorinated species. Only chlorinated benzenes from the degradation of 2,3',4,4',5-pentachlorobiphenyl were major chlorinated products of the spiked sludge.

The major, thermally stable PICs were all aromatic in nature. These included simple benzenoid species such as benzene, toluene, and styrene which were attributed primarily to sludge degradation. Polynuclear aromatic

species were also observed to be stable and produced in significant yields, including naphthalene, indenenes, benzo and dibenzo-furans, 9 H-fluorene, and phenanthrene which are also probably due to sludge degradation. Nitrile containing species such as benzonitrile, 9 H-carbazole, and diphenyldicarbonitrile were among the highest yield stable PICs and apparently resulted from interaction of diphenylamine or azobenzene decomposition products and the sludge.

Compared to previous studies of the thermal degradation of a wide range of waste types, the spiked sludge resulted in a relatively high yield of stable PNAs, aromatic nitriles, and chlorinated aromatic species (14,19). However, we recognized that the wide range of combustion conditions, especially exposure temperature, in a multiple hearth could significantly affect emissions.

Accordingly, a limited set of experiments was run to simulate the stepped increase in exposure temperature of contaminated sludge cascading down the hearths of the drying zone of a multiple hearth incinerator. Specifically, it was expected that bed temperatures on the upper hearths could be high enough to volatilize organic constituents, but that gas phase temperatures might not be high enough to result in their destruction. This simulation was performed by a stepwise increase in the temperature of the insertion region from 50 to 500°C while the reactor temperature was held constant at the virtually non-destructive temperature of 300°C. These data, summarized in Figure 2, graphically display that the majority of the desorbable organics were volatilized below 200°C. This corresponds to the upper hearths of a multiple hearth incinerator, which for a countercurrent flow design, means little destruction would be achieved.

A comparison of potential emission levels from the multiple hearth versus the fluidized bed incinerator is shown in Figure 3. The top chromatogram depicts volatile species desorbed from the sludge and transported through the reactor at 300°C, while the bottom chromatogram shows the remaining species after these volatilized organics have been subjected to an 800°C reactor temperature. While the thermal conditions in the top chromatogram approximate those in the drying zone of the multiple hearth incinerator, those in the bottom chromatogram are more characteristic of the thermal regime in the fluidized bed incinerator. This indicates that the thermal regime of the fluidized bed incinerator may be much less likely than that of a multiple hearth to lead to major gaseous organic emissions.

We were also concerned about the effects of a high bed temperature (and short reaction time at temperature) combined with a long burnout time but low reaction temperature. This would correspond to conditions achieved in a multiple hearth incinerator when non-volatile components of a highly contaminated sludge reach the upper hearths of the combustion zone. Results of sludge pyrolysis experiments at 500°C and 800°C revealed that large quantities of cholesterol-like compounds, PNAs and chlorinated PNAs are formed under these conditions. The cholesterol-like compounds are likely present in the sludge (from bile salts, natural and synthetic hormones, and cell membranes) while the PNAs result from the sludge and sludge/contaminant

Figure 2.

Chromatograms of organics desorbed from sludge in various sample insertion region temperature ranges.

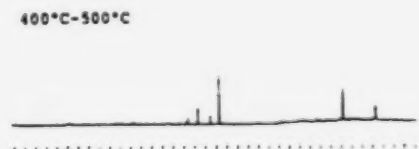
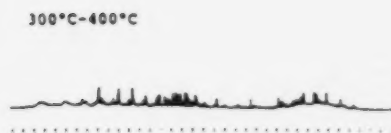
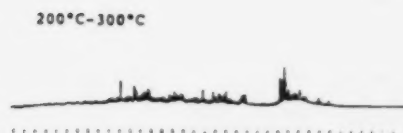
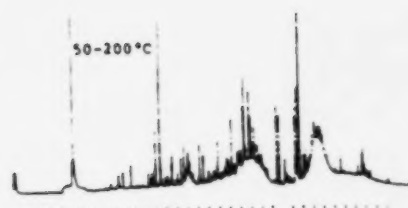
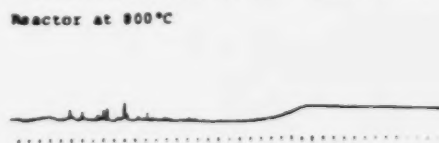
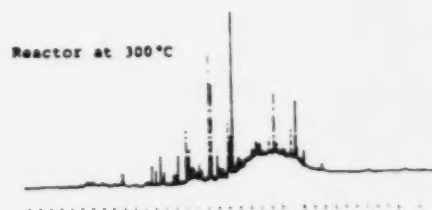


Figure 3.

Comparison of potential emissions levels from a) drying zone of multiple hearth versus; b) fluidized bed incinerator.



interaction. Since these PNAs and chlorinated PNAs are very stable under oxidative or pyrolytic conditions, they are likely to escape destruction in the upper regions of the incineration chamber.

Toxic Emissions Control Implications

Our results suggest that counter-current flow multiple hearth incinerators, as presently operated, may not be sufficient to destroy most organic emissions with even a 99% efficiency. Thus, much higher upper hearth gas phase temperatures must be realized ($>1000^{\circ}\text{C}$) in order to control emissions of volatiles. Even with these controls it may be difficult to control PIC emissions due to the reduced gas phase reaction time experienced by combustion intermediates. Although it is important to increase the gas phase temperature of these systems, it also seems prudent to attempt to strive for gradual heating of the sludge to minimize possible condensed phase pyrolysis or flash volatilization (which causes gas phase pyrolysis due to poor fuel/air mixing) which can result in formation of stable polynuclear aromatic species (20,21).

One solution to this dilemma would be to employ a high-temperature afterburner. Research studies indicate that a system operating at a minimum temperature of 1000°C , $\bar{t}_r = 2.0$ s, and 50% excess air should be sufficient to destroy most toxic emissions (14,18,19).

Regulation and compliance testing would appear to present a difficult challenge because of the multitude of toxic contaminants that could be contained in sewage sludge. One possibility would be to conduct compliance testing for major emissions identified from lab studies or comprehensive research studies conducted on full-scale units. Based on the results of our lab tests benzonitrile, benzene, naphthalene, and benzaldehyde would be appropriate compliance test surrogates that are likely to be "major" trace emissions from any sewage sludge incinerator regardless of contamination. If products specific to the sludge can be identified based on lab studies or theory, those with the highest concentration and stability should also be monitored. The previously developed hazardous waste thermal stability index could be used to guide these selections (14).

The field test results on these compounds could then be used in conjunction with a risk assessment of the stack emissions. This risk analysis should contain all possible emissions identified by laboratory studies, reaction kinetic theory, or field tests. The emissions results for the limited number of compounds from the compliance test could then be compared to theoretical or laboratory based predictions of emission rates and used to "calibrate" the emissions estimates for the other estimated emissions. In this way, a comprehensive, quantitative risk assessment may be conducted.

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CREDIT

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PREDICTED AND OBSERVED ORGANIC EMISSIONS FROM SEWAGE SLUDGE INCINERATION

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ABSTRACT

Samples of sewage sludge burned at three multiple hearth and one fluidized bed incinerator were subjected to laboratory flow reactor thermal decomposition testing under both pyrolytic and oxidative atmospheres. The time/temperature conditions of the laboratory testing were established to simulate as closely as possible full-scale incineration conditions such that a direct comparison of results could be made.

The laboratory test results indicated that biomass decomposition products, not toxic industrial contaminants, comprised the majority of the emissions. Benzene, toluene, ethylbenzene, acrylonitrile, and acetonitrile were consistently the most environmentally significant products of thermal exposure. Quantitative comparison of emission factors derived from lab and field results for those compounds observed in both studies showed excellent correlation for the pyrolysis testing. Rank/order correlations were statistically significant at the 95% confidence level for all four sources. This study suggests pyrolysis pockets of poor fuel/air mixing in the full-scale incinerators may have been responsible for many of the observed combustion by-products.

INTRODUCTION

Results of recent field tests on sewage sludge incinerators have shown that a number of toxic products of incomplete combustion (PICs) may be emitted from multiple hearth and fluidized bed units (1-3). This raised some concerns and suggests that a better understanding of the nature of these emissions be developed before adequate regulatory and control strategies be undertaken.

We have recently participated in a comparison of the results of bench scale thermal decomposition testing of four sewage sludge samples with results of a full-scale incineration test program conducted by Radian Corporation under US-EPA sponsorship (4-10). Three multiple hearth units and one fluidized bed facility were chosen for examination (c.f. Table 1.)

TABLE 1. DESIGN PARAMETERS OF SELECTED SEWAGE SLUDGE INCINERATORS

Design Parameter	Site 1	Site 2	Site 3	Site 4
Type	Multiple Hearth 6 Hearths	Multiple Hearth 8 Hearths	Fluidized Bed 5 ft. sand depth 22 ft. diameter	Multiple Hearth 6 Hearths
Source	Domestic	Industrial and Domestic	Municipal	Industrial and Domestic
Exit O ₂ Conc (min)	10%	6%	9-12%	7-10%
Combustion Zone	1500-1600°F (815-870°C)	1300-1600°F (704-870°C)	1350-1400°F (732-760°C)	1100-1700°F (593-926°C)

EXPERIMENTAL

Thermal decomposition testing for all four of the sewage sludge samples was conducted using the System for Thermal Diagnostic Studies (STDS) (10,11). This instrumentation assembly permits the study of the thermal decomposition of gaseous, liquid, solid, or polymeric substances under very precise conditions. Thermal decomposition experiments can be conducted in a variety of atmospheres with residence times varying from 0.1 - 10 seconds. An in-line GC-MS system provides for analysis of the effluent resulting from thermal exposures.

Using combinations of insertion region programming and reactor temperature, the multiple hearth incinerator simulation was divided into four progressive steps. The first and second steps were designed to simulate the drying zone of the incinerator (i.e., the sludge was exposed to temperatures ranging from 50-450°C); the third and fourth steps were designed to simulate the combustion zone of the incinerator (i.e., the sludge was exposed to temperatures of 450-800°C). GC-MS analysis was performed at the end of each step in this process. The individual contributions were then summed to provide for the total emissions coming from laboratory simulated 'incineration' of the sludge sample. It was this data which was compared to full-scale emissions data for each of the three sites.

Simulation of the fluidized bed unit required only a single step with rapid heating of the sludge to 700°C in the insertion region followed by a downstream reactor exposure of 700°C. GC-MS techniques were again employed to perform analysis of the reactor effluent. Laboratory data from this exposure was then compared with full-scale data from the single fluidized bed facility.

RESULTS

Full-scale experiments showed that greater than 99% of the mass emissions from the thermal decomposition of all four sludges resulted from the decomposition of the biomass of the sludge itself. Many long-chain carboxylic acids, ketones, aldehydes, amino acids, etc., were detected. Even the two most common emissions seen from all four sludges, benzene and toluene, were more a result of the thermal decomposition of the biological material present in the sludge than from any initial contamination in the feed itself. This phenomenon was observed in previous studies on sludges from different sites (12).

Sulfur containing compounds were only observed in laboratory tests for Sites 2 and 3. Perhaps the industrial contribution to the influent waste stream in both cases was responsible for the sulfur-containing emissions.

The reactor effluent for the laboratory fluidized bed sample from Site 3 was notably much cleaner in terms of number and relative yield of products than observed for the three multiple hearth samples. This is as one might expect based on the more uniform combustion provided for in the simulated fluidized bed experiments.

A comparison of laboratory and field test results are presented in Table 2. This comparison is complicated by the difficulty of conducting chemical analysis for specific toxic materials within an overwhelming organic matrix as background. Both laboratory and field studies were subject to this difficulty. As a result, the joint program concentrated upon detection of specific toxics contained in a generic 'target list' which are enumerated in Table 2. Compounds were selected based upon toxicity, suspected prevalence in sewage sludge, and representativeness of different classes of potential pollutants. Compounds were also added to the 'target list' based upon their detection in a preliminary round of laboratory testing of sludges from the four test sites which was completed before full-scale testing was begun. This initial testing allowed for the addition of major 'site specific' emissions to the generic 'target list'.

TABLE 2. COMPARISON OF 'TARGET LIST' COMPOUNDS DETECTED IN FULL-SCALE AND LABORATORY TESTING

	Site 1		Site 2		Site 3		Site 4	
	Field	Lab	Field	Lab	Field	Lab	Field	Lab
Acrylonitrile	X(1)	X	Xw	X	X	(2)	X	X
Benzene	X	Xs	X	X	Xs(3)	Xs	Xs	Xs
Carbon Tetrachloride	X		X		Xs		X	
Chlorobenzene	X		Xs		Xs		X	
Chloroform	Xw		Xw(4)		Xs&w		Xs&w	
1,2-Dichloroethane	X						na	
1,2-Dichloroethene	X		X				Xs&w	
Ethylbenzene	X	X	Xs	Xs	Xs		Xs	X
Methylene Chloride	X		Xs&w		Xs&w		Xs&w	
Tetrachloroethylene	Xs&w		X		Xs	Xs	Xs&w	Xs
Toluene	X	X	Xs	Xs	Xs	Xs	Xs	Xs
1,1,1-Trichloroethane	X		X		Xs		Xs&w	Xs
Trichloroethylene	X		X		Xs		Xs&w	
Vinyl Chloride	X	na(6)	X	na		na	X	na
Acetonitrile	na(5)	na	na	na	na	na	X	X
2-Butanone(MEK)	na	na	na	na	na	na	X	X
Pyridine	na	na	na	na	na	na		
Phenol	X	X	X		s		X	X
Naphthalene	na	na	Xs		na	na	Xs	X
2-Nitrophenol			X		na	na		
1,2-Dichlorobenzene	X		X		na	na		
1,3-Dichlorobenzene	X		X		s			
1,4-Dichlorobenzene	X		X		s			

1. 'X' indicates compound was detected in effluent from stack or from thermal testing
2. 'blank' indicates compound was analyzed for, but was not found in effluent
3. Subscript 'w' denotes compound was detected in the scrubber inlet water
4. Subscript 's' denotes compound was detected in the sludge feed
5. 'na' indicates that compound was not included in 'target list' for that facility
6. Vinyl chloride was not included in laboratory testing

Site 1

Previously performed laboratory studies of the oxidative pyrolysis of pure tetrachloroethylene have shown that carbon tetrachloride is formed as a PIC (13). These experiments also showed that given a hydrogen source, trichloroethylene was readily formed as a PIC from tetrachloroethylene. The radical pool generated during the incineration of municipal sludge would provide such a source of hydrogen. Thus, if tetrachloroethylene were present in a sludge stream, both trichloroethylene and carbon tetrachloride would likely be detected in the stack effluent. Full-scale data generated in this program correlated with this laboratory finding; tetrachloroethylene was detected in the sludge feed sample collected during the full-scale testing and carbon tetrachloride and trichloroethylene were found in the stack. However, tetrachloroethylene was not detected in the sludge feed sample furnished for the laboratory study, as evidenced by its absence

in the 300°C run; nor were any other chlorinated compounds detected. This resulted in no chlorinated products being observed.

This was a reoccurring problem throughout the test program. Although precautions were taken, it is possible that the small sample furnished for laboratory analysis was not truly representative of the sludge feed, or that the volatile organic content of the laboratory samples was lost during transit or cold storage, or that microbial anaerobic degradation occurred.

Site 2

In the feed samples collected during full-scale testing from Site 2, two chlorinated compounds, methylene chloride and chlorobenzene, were found which were not detected in the sample provided for laboratory testing. In previous laboratory experiments we have found that 1,1-dichloroethylene, 1,2-dichloroethylene, and trichloroethylene were all formed as products from the pyrolytic decomposition of pure methylene chloride (14). Thus, it is not surprising that a facility incinerating sludge contaminated with methylene chloride had these compounds present in its emissions. Since no methylene chloride was present in the laboratory sludge feed sample, these products could not be expected to be detected. In fact, no chlorine-containing compounds were detected in the sludge sample provided for laboratory testing. This explains the absence of chlorine-containing compounds in the effluent from thermal testing of this sample.

The chlorobenzene detected in the stack emissions at this facility probably resulted from a combination of two processes. The first is the original contamination found in the sludge feed. Previous studies have shown chlorobenzene to be a very stable compound, even when decomposed as part of a mixture (15,16). Thus, the appearance of chlorobenzene in the stack is probably due, in part, to the ability of this compound to undergo relatively harsh thermal exposures and escape unscathed. The second contribution to the emission of chlorobenzene at the full-scale facility is the possibility that this compound was formed as a PIC. We have conducted many studies involving the decomposition of benzene and/or toluene or related compounds in the presence of chlorinated species. The free chlorine radicals generated in such a reaction atmosphere have combined with phenyl radicals to produce chlorobenzene in almost every case (16). Because a host of chlorine containing compounds were detected in the sludge feed at the full-scale facility, it is logical that chlorobenzene was detected in the stack.

Two products seen in full-scale emissions, tetrachloroethylene and 1,1,1-trichloroethane, may be the result of a slightly more complex scenario. Tetrachloroethylene is a frequent product observed from the oxygen deficient decomposition of various chlorinated materials as mixtures or pure compounds (17). It has proven to be a stable compound when seen as a PIC. In fact, significant levels of tetrachloroethylene were still present in one laboratory study at temperatures above 900°C, making this compound one of the most stable PICs observed in any experiments we have conducted. Thus, it is conceivable that a decomposition atmosphere containing some of these compounds could have produced tetrachloroethylene as a PIC.

The emission of 1,1,1-trichloroethane is surprising due to its previously demonstrated thermally fragile nature (18). For it to be emitted from the incinerator as a PIC, it would have to be formed near the exit of the high temperature zone and its decomposition rapidly quenched. Recombination of methyl radicals and trichloromethyl radicals is the most likely mechanism of formation. Since chloroform is the best source of trichloromethyl radicals detected, and it was in the scrubber water, it is most likely that the 1,1,1-trichloroethane was formed outside the combustion zone of the incinerator. The proposed reaction requires temperatures high enough to decompose chloroform (approximately 500°C), presumably from quenching of hot gases in the scrubber, followed

by methyl-trichloromethyl radical recombination. Alternatively, a liquid phase reaction must be invoked.

Finally, methylene chloride and chloroform were both seen as contaminants in the scrubber water at the Site 2 facility. This explains their presence in that facility's emissions during full-scale testing and their presence in the lab tests. Acrylonitrile was also detected in the scrubber water at the Site 2 facility, but its presence in the stack cannot be attributed exclusively to this phenomenon. The compound was seen at the pollution control device inlet for this facility, indicating that it was formed as a PIC in the incineration of the Site 2 sludge. Laboratory thermal testing reproduces this finding.

Site 3

Many hit list compounds were observed in the full-scale analyses of the sludge feed at the fluidized bed facility. All of these compounds were subsequently detected in emissions from full-scale testing conducted at this facility: benzene, carbon tetrachloride, chlorobenzene, chloroform, ethylbenzene, methylene chloride, tetrachloroethylene, toluene, trichloroethylene, and 1,1,1-trichloroethane. Analysis of the sample provided for laboratory testing found only benzene, toluene, and very low levels of tetrachloroethylene, while only benzene and toluene were detected as products in the effluent from laboratory thermal experiments.

However, it is important to note that the emission factors (in units of mg emitted/metric ton of combustibles fed) reported from the Site 3 facility show that all but a few of the compounds were present in the stack at low levels (i.e., less than an emission factor (EF) of 100). Only benzene, chloroform, methylene chloride and toluene had EF values greater than 100. Of these, chloroform and methylene chloride were contaminants of the scrubber water. Laboratory testing duplicated full-scale results for those compounds with field EFs of greater than 100, except for those compounds whose EFs were an indication of their contamination in the scrubber water.

Site 4

Full-scale analysis reported methylene chloride, 1,2-dichloroethylene, benzene, chloroform, ethylbenzene, tetrachloroethylene, toluene, 1,1,1-trichloroethane, trichloroethylene, and naphthalene to be contaminants of the original sludge feed for the facility at Site 4. All of these compounds except 1,2-dichloroethylene were subsequently observed in stack emissions. Laboratory analysis of the Site 4 sample only documented the presence of benzene, toluene, tetrachloroethylene and 1,1,1-trichloroethylene. Of these benzene, toluene, and small levels of tetrachloroethylene were seen in the emissions from laboratory thermal testing. Naphthalene was also detected in laboratory testing, although it was not detected in the original sludge feed sample as was the case for full-scale testing.

Full-scale testing also showed acetonitrile, acrylonitrile, carbon tetrachloride, chlorobenzene, 2-butanone (MEK) and phenol to be present in full-scale emissions. These compounds were undoubtedly formed *in situ*. Laboratory testing of the Site 4 sample reproduced detection of benzene, toluene, naphthalene, acrylonitrile and phenol.

The presence of tetrachloroethylene and 1,1,1-trichloroethane in the full-scale and the laboratory sludge feed samples (9,10) would predict that carbon tetrachloride and chlorobenzene should be found in the emissions from full-scale and laboratory testing of this sludge for reasons outlined previously. In fact, full-scale results did show carbon tetrachloride and chlorobenzene to be part of the stack emissions from the facility at Site 4. However, testing of the laboratory sludge sample from the same site did not include these compounds. Comparison of the analytical detection limits between laboratory and field testing showed that laboratory detection limits were only slightly higher than those reported

for the full-scale testing. Therefore, it is possible that lower initial concentrations of parent materials (tetrachloroethylene and 1,1,1-trichloroethane) in the laboratory feed sample did not permit sufficient conversion to products so that the analytical detection limits could be surpassed for detection of carbon tetrachloride or chlorobenzene.

DISCUSSION

The apparent loss of chlorinated compounds from the sludge samples for whatever reasons clearly complicated field/lab comparisons. As a result we conducted a statistical comparison of the relative emissions for only those compounds observed in both the laboratory and field testing. Table 3 presents a ranking of the relative rate of these emissions from highest to lowest, as well as a listing of the relative emission factors (REFs) for each of these compounds. Subjecting the ranked pairs of field/lab data to the Wilcoxin Rank Sum Test (19) provided interesting results. In all three cases amenable to statistical analysis the rankings of highest to lowest emissions exhibited a statistically significant agreement. Site 3 could not be examined in this manner since there were insufficient data.

TABLE 3. RANKING OF TOP EMISSIONS FOR COMPOUNDS QUANTITATED IN FULL-SCALE AND LABORATORY TESTING

Compound	Ranking		Relative Emission Factors (relative to benzene)	
	Field	Lab	Field	Lab
Site 1:				
Acrylonitrile	2	2	0.350	0.836
Benzene	1	1	1	1
Toluene	3	4	0.301	0.015
Ethylbenzene	4	3	0.101	0.638
Site 2:				
Acrylonitrile	1	1	2.40	2.03
Toluene	2	2	2.36	1.66
Benzene	3	3	1	1
Ethylbenzene	4	4	0.100	0.311
Site 3:				
Benzene	1	1	1	1
Toluene	2	2	0.160	0.120
Site 4:				
Acetonitrile	1	3	5.20	0.130
Acrylonitrile	3	2	3.33	0.147
Benzene	4	1	1	1
MEK	5	6	0.330	<0.005
Ethylbenzene	6	5	0.122	0.016
Toluene	2	4	4.44	0.020

We also conducted a comparison of the observed average emission of all compounds ('hit list' and observed semi-volatiles) in the full-scale testing from all sites versus predicted emissions based on a large previously generated data base on stability of organic compounds (20-22). The full-scale destruction efficiencies (DEs) for each species were ranked and compared to the destruction efficiencies predicted based purely on our previously developed thermal stability based ranking of toxic organic compound incinerability (20). Since many of the emissions were clearly due to PIC formation, a second comparison was made wherein the predicted contribution due to PIC formation was included (21,22). Principles of elementary reaction kinetics and available lab data were used to estimate PIC yields (21-23). The impact on measured DE depends on the concentration of the species in the feed. Those compounds with low feed concentrations are subject to large effects from PIC formation, while the measured DE of those compounds with high feed concentration are only affected by PIC formation if the PIC yield is very high. Figure 1 presents a correlation summary of these two comparisons: 1) theoretical stability-

vs-observed destruction efficiency and 2) theoretical stability plus PIC formation propensity- vs-observed destruction efficiency.

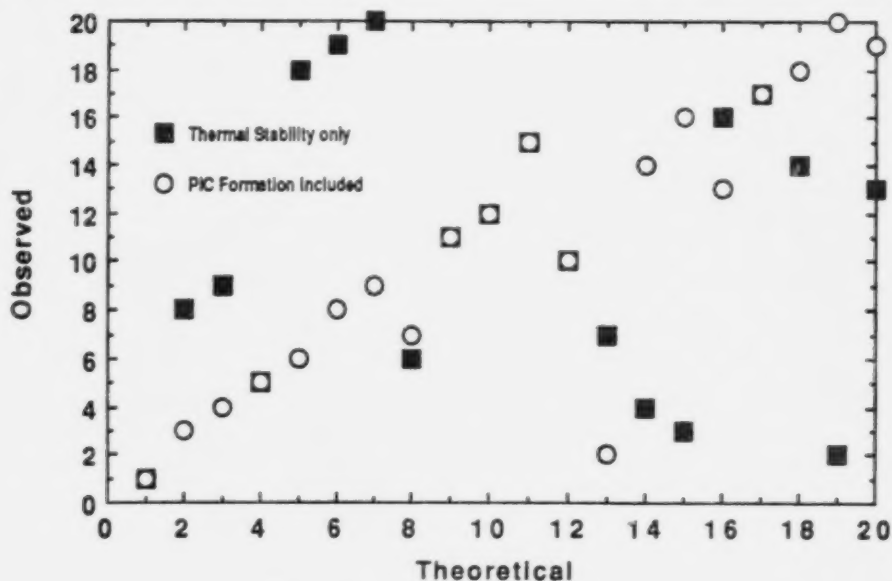


Figure 1 - Theoretically Predicted-vs-Actual Pollutant Emission Ranking

As can be seen, excellent correlation was obtained when PIC considerations were included in the theoretical ranking of thermal stability, whereas poor correlation was observed when theoretical stability alone was compared with observed stability. The Spearman Coefficient of Rank correlation test resulted in a 99.5% confidence interval for correlation between field data and theoretical predictions when PIC formation was included. Only chloroform showed a major deviation. However, this is not surprising since chloroform was found in the scrubber water at many facilities. Stripping of this compound from the water and subsequent emission in the stack accounts for its seemingly high 'observed' ranking.

SUMMARY AND CONCLUSIONS

This was the first time that a direct comparison has been attempted using an actual waste sample for laboratory analysis which was incinerated at a full-scale facility. In spite of the complexity of the program, the comparison of results for major PIC emissions was remarkably good. Future work should include a plan for immediate comparison of the chemical analysis results for samples collected for laboratory and field testing to ensure that a true comparison of emissions between the two studies may be guaranteed (i.e., to ensure that both studies will be working with the same starting material).

Emission factors (mass emitted/mass fed units) were used in this study as a basis of comparison between laboratory and field data. The full-scale emission factors were generated with data taken at the outlet of a pollution control device, while laboratory data might have been more analogous to full-scale data taken at the inlet to the pollution control device. This is because the product effluent generated in laboratory thermal testing does not get 'scrubbed'. In the future, it would be advisable to compare full-scale emissions at the inlet of the pollution control device with those obtained in laboratory thermal testing to

see if these comparisons will provide a better correlation. This type of comparison was not possible for this study.

The laboratory data generated in nitrogen agreed best with full-scale data. This is consistent with the previously proposed theory that most 'combustion' emissions are actually due to pyrolysis in small oxygen deficient pockets of gases (23). In fact, a previously proposed pyrolytic thermal stability index of toxic waste incinerability in conjunction with estimates of PIC emission predicted full-scale emission test results with remarkable accuracy (24).

The development of an a priori 'target list' is a valuable first step towards determining potential toxic organic emissions from sewage sludge incinerators. This necessarily requires that one suspect a particular compound to be present. However, more research is clearly necessary before we can ensure that all potentially toxic emissions are being addressed. One possible technique for developing a more comprehensive full-scale emissions test approach would be to conduct laboratory thermal decomposition testing on spiked sludges. By adding higher levels of toxic organic contaminants and PIC precursors to the sludge, trace toxic emissions can be more readily and comprehensively identified to guide full-scale testing and monitoring.

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CHARACTERIZATION OF MUNICIPAL WASTE
COMBUSTION ASHES AND LEACHATE
FIELD STUDY RESULTS

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ABSTRACT

Incineration of MSW has become an important alternative to the land disposal of MSW. Incineration is an effective means of reducing the volume of MSW and can provide an important source of energy. Ash from the combustion of household waste has been excluded from regulations under Subtitle C of RCRA, which regulated disposal of hazardous wastes. However, in some instances testing the residues from municipal waste incinerators by the Extraction Procedure (EP) Toxicity test is being required to determine if these residues would be classified as hazardous waste and, therefore, subjected to disposal regulations under Subtitle C. Ashes from MWC facilities, on occasion, have exhibited hazardous waste characteristics as determined by the EP Toxicity test. The debate regarding the representativeness and the validity of this test and the relation of these results to actual leachates from ash disposal facilities has not been settled.

For this reason, EPA and CORRE have cosponsored a study designed to enhance the data base on the characteristics of MWC ashes, laboratory extracts of MWC ashes, and leachates from MWC ash disposal facilities. Ash samples were collected from 5 MWC facilities and leachate samples were collected from the companion ash disposal sites. These ash and leachate samples were analyzed for the Appendix IX semivolatile compounds, polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), metals for which Federal primary and secondary drinking water standards exist, and several miscellaneous conventional compounds. The ash samples were also subjected to six laboratory extraction procedures and the extracts were then analyzed for the same compounds as the ash samples. All sampling, laboratory preparation, and laboratory analysis followed stringent quality assurance/quality control (QA/QC) procedures.

The major findings of this study are described in this paper.

INTRODUCTION

This paper provides a summary of the findings provided in a recent report which has been prepared for the United States Environmental Protection Agency (EPA) and the Coalition on Resource Recovery and the Environment (CORRE). EPA and CORRE have cosponsored this study to enhance the data base on the characteristics of MWC ashes, laboratory extracts of MWC ashes, and leachates from MWC ash disposal facilities.

The Coalition on Resource Recovery and the Environment (CORRE) was established to provide credible information about resource recovery and associated environmental issues to the public and to public officials. In providing information, CORRE takes no position as to the appropriateness of one technology compared to others. CORRE recognizes that successful waste management is an integrated utilization of many technologies which taken as a whole, are best selected by an informed public and informed public officials.

Incineration of municipal solid waste (MSW) has become an important waste disposal alternative because it provides an effective means of reducing the volume of MSW as well as an important source of energy recovery. Currently, 10 percent of the United States MSW is incinerated. Based on the number of municipal waste combustion (MWC) facilities being planned across the country, this percentage is expected to increase to 16-25 percent by the year 2000.

As incineration of MSW has increased in recent years, so has concern over its management. To resolve the many legal and technical issues surrounding ash, Congress is considering several legislative initiatives that would classify municipal waste combustion (MWC) ash as a special waste under Subtitle D of the Resource Conservation and Recovery Act (RCRA) and require the Environmental Protection Agency (EPA) to develop special management standards for the full life cycle of ash. In anticipation of Congressional action, EPA and the Coalition on Resource Recovery and the Environment (CORRE) cosponsored this study to characterize ash and to gain a better understanding of how it behaves in the environment.

DESCRIPTION OF STUDY

Combined bottom and fly ash samples were collected from five mass-burn MWC facilities and leachate samples were collected from the companion ash disposal sites.

The facilities sampled were selected by CORRE to meet the following criteria:

- o The facilities were to be state-of-the-art facilities equipped with a variety of pollution control equipment.
- o The facilities were to be located in different regions of the United States.
- o The companion ash disposal facilities were to be equipped with leachate collection systems or some means of collecting leachate samples.

The identities of the facilities are being held in confidence.

The ash and leachate samples collected were analyzed for the Appendix IX semivolatile compounds, polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs), metals for which Federal primary and secondary drinking water standards exist, and several miscellaneous conventional compounds. In addition, the ash samples were analyzed for major components in the form of oxides.

The ash samples were also subjected to six laboratory extraction procedures and the extracts were then analyzed for the same compounds as the original ash samples. The following six extraction procedures were used during this study:

- o Acid Number 1 (EP-TOX)
- o Acid Number 2 (TCLP Fluid No. 1)
- o Acid Number 3 (TCLP Fluid No. 2)
- o Deionized Water (Method SW-924), also known as the Monofill Waste Extraction Procedure (MWEP)
- o CO₂ saturated deionized water
- o Simulated acid rain (SAR)

These extraction procedures have been used separately by a variety of researchers on MWC ashes but never have all six procedures been used on the same MWC ashes. This was intended to compare the analytical results of the extracts from all six procedures with each other and with leachate collected from the ash disposal sites used by the MWC facilities.

All sampling, laboratory preparation, and laboratory analysis followed stringent EPA quality assurance/quality control (QA/QC) procedures. The detection limits of the analytical methods used were well below present levels of human, environmental, or regulatory concerns.

The EPA publication "Interim Procedures for Estimating Risk Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs)" was used to evaluate the dioxin data. These procedures use Toxicity Equivalency Factors (TEFs) to express the concentrations of the different isomers and homologs as an equivalent amount of 2,3,7,8-Tetrachloro Dibenzo-p-Dioxin (2,3,7,8-TCDD). The Toxicity Equivalents, as calculated by using the TEFs, are then totaled and compared to the Centers for Disease Control (CDC) recommended upper level of 2,3,7,8-TCDD Toxicity Equivalency of 1 part per billion in residential soil.

The major features of the five MWC facilities and ash sites sampled are provided in Table 1, and Table 2 respectively. Pertinent information on the operating conditions of the MWC facilities, as well as information about the air pollution control equipment used is also provided in Table 1.

STUDY RESULTS AND CONCLUSIONS

Major findings of and conclusions drawn from the results obtained from the sampled ash, natural leachates, and laboratory extracts are summarized in the paragraphs which follow.

Ash Analysis Results

Of the five ash samples (one from each facility) analyzed for the Appendix IX semivolatile compounds, four samples contained bis(2-ethylhexyl)phthalate, three contained di-n-butyl phthalate, and one contained di-n-octyl phthalate. Two PAHs, phenanthrene and fluoranthene, were detected in only one of the five ash samples. These semi-volatile compounds were detected in the parts per billion (ppb) range.

The results for the ash samples analyzed for PCDDs/PCDFs are presented in Table 3. This table also includes the calculated Toxicity Equivalents (TE) for each homolog of PCDD/PCDF. The data indicate that PCDDs/PCDFs were found at extremely low levels in each of the ash samples. The Total TE for each ash

sample was well below the Centers for Disease Control (CDC) recommended Toxicity Equivalency limit of 1 part per billion 2,3,7,8-TCDD in residential soil.

All 25 of the ash samples (five daily composites from each facility) were analyzed for the metals listed on the primary and secondary drinking water standards as well as for the oxides of five major ash components. Although, the results from these analyses indicate that the ash is heterogeneous, this heterogeneity appears to have been reduced by the care taken when compositing the ash samples during this study. Data from this study showed less variability than comparable data in the literature.

Metals showing the widest range of concentrations among samples collected at each facility included barium (ZB); cadmium (ZB); chromium (ZD, ZE); copper (ZA, ZB, ZC); lead (ZD); manganese (ZA, ZC); mercury (ZE); zinc (ZB, ZD, ZE); and silicon dioxide (ZA).

Metals showing the widest variation of concentrations between the facilities included barium (results for Facility ZC are lower than the results for the other facilities); iron (results for each facility vary from all of the other facilities); lead (results for Facility ZD are higher than the results for the other facilities); mercury (results for Facilities ZC and ZD are lower than the results for the other facilities); sodium (results for Facilities ZD and ZE are lower than the results for the other facilities); calcium oxide (the results for Facilities ZA and ZB are higher than the results for the other facilities); and silicon dioxide (the results for Facility ZC are higher than the results for the other facilities).

Some additional findings of the ash sampling and analyses are as follows:

- o The ashes are alkaline with the pH ranging from 10.36 to 11.85.
- o The ashes are rich in chlorides and sulfates. The total soluble solids in the ashes varied from 6,440 to 65,800 ppm.
- o The ashes contained unburnt total organic carbon (TOC) ranging from 4,060 ppm (0.4 percent) to 53,200 ppm (5.32 percent).

Leachate Analysis Results

Only four Appendix IX semivolatile compounds were found in the leachates. Benzoic acid was found in two leachate samples collected at one site. Phenol, 3-methylphenol, and 4-methylphenol were found in the leachate samples from another site. All of these compounds were detected at very low levels (2-73 ppb).

PCDDs/PCDFs of the higher chlorinated homologs were found in the leachate from one site only. This indicates that PCDDs/PCDFs do not readily leach out of the ash. The low levels found in the leachates of the one site probably originated from the solids found within the leachate samples because these samples were not filtered nor centrifuged prior to analysis.

The metal content in the leachate samples did not exceed the EP Toxicity Maximum Allowable Limits established for the eight metals in Section 261.24 of 40 CFR 261. Indeed, the data indicate that although the leachates are not used as a source of potable water, they are close to being acceptable as such as far as the metals are concerned.

Other observations on the leachate analyses are:

- o Sulfate values ranged from 14.4 mg/L to 5,080 mg/L, while Total Dissolved Solids (TDS) ranged from 924 mg/L to 41,000 mg/L.
- o The field pH values ranged from 5.2 to 7.4.
- o Ammonia (4.18-77.4 mg/L) and nitrate (0.01-0.45 mg/L) were present in almost all leachate samples.
- o Total Organic Carbon values ranged from 10.6 to 420 ppm.

Ash Extracts Analysis Results

The data obtained during the metals analyses of the ash extracts indicate, in general, that the extracts from the EP Toxicity, the TCLP 1, and the TCLP 2 extraction procedures have higher metals content than the extracts from the deionized water (SW-924), the saturated CO₂ solution, and the Simulated Acid Rain (SAR) extraction procedures.

The EP Toxicity Maximum Allowable Limits for lead and cadmium were frequently exceeded by the extracts from the EP Toxicity, TCLP 1, and TCLP 2 extraction procedures. One of the extracts from the EP Toxicity extraction procedure also exceeded the EP Toxicity Maximum Allowable Limit for mercury.

None of the extracts from the deionized water (SW-924), the saturated CO₂ solution, and the Simulated Acid Rain (SAR) extraction procedures exceeded the EP Toxicity Maximum Allowable Limits. In addition, all of the extracts from these three extraction procedures also met the Primary and Secondary Drinking Water Standards for metals.

Table 4 compares the range of concentrations of the metals analyses of the ash extracts with the range of concentrations for leachate as reported in the literature and the range of concentrations for the leachates as determined in this study. For the facilities sampled during this study, the data in Table 4 indicate that the extracts from the deionized water (SW-924), the saturated CO₂ solution, and the SAR extraction procedures simulated the concentrations for lead and cadmium in the field leachates better than the extracts from the other three extraction procedures.

Additional observations are:

- o Of the five composite samples of the deionized water (SW-924) extracts analyzed for the Appendix IX semivolatile compounds (one from each facility), only one sample contained low levels of benzoic acid (0.130 ppm).
- o None of the extracts contained PCDDs/PCDFs. These data confirm the findings of the actual field leachate samples that PCDDs/PCDFs are not leached from the ash.

TABLE 1

MAJOR FEATURES OF MWC FACILITIES

Operational Features	Facilities				
	ZA	ZB	ZC	ZD	ZE
Facility Type	Energy recovery, continuous feed, reverse-reciprocating grate	Energy recovery, continuous feed, reciprocating grate	Energy recovery, continuous feed, reverse-reciprocating grate	Energy recovery, continuous feed, reciprocating grate	Energy recovery, continuous feed, reciprocating grate
Startup Date	May 1985	Early 1987	January 1987	1975	September 1987
Capacity	275 tons/day/boiler 2 boilers	75-100 tons/day/boiler 2 boilers	400 tons/day/boiler 3 boilers	750 tons/day/boiler 2 boilers	750 tons/day/boiler 2 boilers
Combustion Temperature	1,800-2,000°F at stack	1,800°F	1,750-1,800°F	1850-1925°F (fly ash at 1850°F)	1,800°F at the grate
Temperature of air entering the boiler	Under fire: 250°F Over fire: ambient	Under fire: ambient Over fire: ambient	Under fire: 280°F Over fire: ambient	Under fire: ambient Over fire: ambient	Under fire: ambient Over fire: ambient
Volume of air entering boiler	Under fire: 70,000-80,000 lb/hr Over fire: 61,000 lb/hr	Under fire: 45,000 cu ft/hr Over fire: 5,900 cu ft/hr	Under fire: 11,000 lb/hr Over fire: 11,000 lb/hr	Under fire: 11,000 lb/hr Over fire: 11,000 lb/hr	Under fire: 11,000 lb/hr Over fire: 11,000 lb/hr
Source of air quench water	Floor drains, rain water	Carling tower and boiler blowdown, septic system discharge, floor drains	Furnace (oil) and room neighboring sewage treatment plant	Carling tower and boiler blowdown	Carling tower and boiler blowdown
Air pollution control equipment	Lime slurry is injected into flue gas after economizer, fabric filter baghouses.	Dry lime is injected into flue gas after economizer, fabric filter baghouses.	Electrostatic precipitator	Electrostatic precipitator	Lime slurry is injected into flue gas after economizer, electrostatic precipitator
		Fly ash has phosphoric acid added to it and is agglomerated before being mixed with bottom ash.			Fly ash has water added to it and is agglomerated before being mixed with bottom ash.
Approximate waste composition	Residential/Commercial/Light Industrial: 40%	Residential/Commercial/Light Industrial: 80%	Residential/Commercial/Light Industrial: 60%	Residential/Commercial/Light Industrial: 90%	Residential/Commercial/Light Industrial: 65%

TABLE 1
MAJOR FEATURES OF MWC FACILITIES
PAGE TWO

Operational Features	Facilities				
	ZA	ZB	ZC	ZD	ZE
Amount of electricity generated	13.1 megawatts/hour	4.5 megawatts/hour	29 megawatts/hour	35 megawatts/hour	45 megawatts/hour
Amount of electricity used internally by facility	1.7 megawatts/hour	0.63 megawatts/hour	2.5 megawatts/hour	2.5 to 3.5 megawatts/hour	7 megawatts/hour
Material removed from incoming/refuse	Large appliances, other unacceptable material diverted to demolition landfill	Large appliances, material that will not pass through the boilers	Large appliances, material that will not pass through the boilers	Large appliances, material that will not pass through the boilers	Large appliances, material that will not pass through the boilers
Material removed from ash	Ferrous metal removed from ash at the MWC facility	None	Ferrous metal removed from ash at the MWC facility	Ferrous metal removed from ash at the MWC facility	Items greater than 10 inches in diameter

TABLE 2
MAJOR FEATURES OF MWC ASH DISPOSAL FACILITIES

Operational Features	Facilities				
	ZA	ZB	ZC	ZD	ZE
Facility Type	Monofill - single clay liner	Monofill - double liner (HDPE and compacted till soil)	Codisposed facility - bottom-clay liner synthetic sidewall liners	Monofill - unlined Ash is placed over trash deposited before 1975	Monofill - double liner (HDPE and clay)
Startup Date	1986	October 1988	Landfill - 1984 Ash Disposal - 1985	1975	1987
Disposal Capacity	83,400 cubic yards	90,000-100,000 tons	Total capacity 9 million tons	Remaining capacity - 990,000 tons (6 years)	Permitted for 20 years, approximately 3.8 million tons
Amount of Ash Disposed	150 tons/day	60 tons/day	400,000 tons/year 40% ash (2/3 of ash from ZC MWC facility)	450 tons/day	525 tons/day
Materials other than Ash disposed of	None	None	Non-burnable materials from 2 MWC facilities Overflow from 2nd MWC facility	None	None
Leachate Collection System	Perforated PVC pipe in a coarse aggregate envelope	Slotted HDPE	Main header - PVC collection trenches - gravel with fabric filter	None - leachate samples were collected from well points installed in the ash	Slotted HDPE
Cover	Final cover - soil and HDPE	Daily cover - sand. Non working face covered by plastic to limit leachate generation	Daily - native soil and shredded tires Intermediate - native soils Final - native soils	Daily cover - soil. Intermediate - soil compacted to 10% permeability Final - clay or HDPE	Daily cover - soil Intermediate - soil compacted to 10% permeability Final - clay or HDPE
Compaction of Ash	Only as bulldozer spreads ash in ash fill.	Bulldozer spreads and compacts ash in 8-12 inch lifts.	Track mounted compactor	Only as bulldozer spreads ash in ash fill.	Vibrating roller.

TABLE 3

ASH DIOXIN RESULTS

Compound	Toxicity Equivalency Factor (TEF) ⁽¹⁾	Samples (pg/g or ppt)									
		ZA-AH-003		ZB-AH-001		ZC-AH-003		ZD-AH-003		ZE-AH-003	
		Value	Toxicity Equivalents	Value	Toxicity Equivalents	Value	Toxicity Equivalents	Value	Toxicity Equivalents	Value	Toxicity Equivalents
2,3,7,8-TCDD	1	10	10	24	24	16	16	35	35	10	10
Other TCDD	0.01	206	2.06	351	3.51	281	2.81	541	5.41	120	1.2
2,3,7,8-TCDF	0.1	263	26.3	617	61.7	236	23.6	626	62.6	176	17.6
Other TCDF	0.001	1,688	1.69	3,721	3.72	1,208	1.21	2,633	2.63	1,136	1.14
1,2,3,7,8-PCDD	0.5	33	16.5	118	59	71	35.5	ND	0	35	17.5
Other PCDD	0.005	317	1.59	759	3.80	1,051	5.26	1,910	9.55	248	1.24
1,2,3,7,8-PCDF	0.1	61	6.1	194	19.4	64	6.4	151	15.1	52	5.2
2,3,4,7,8-PCDF	0.1	46	4.6	162	16.2	56	5.6	171	17.1	43	4.3
Other PCDF	0.001	484	0.484	1,527	1.53	607	0.607	1,736	1.74	448	0.448
1,2,3,4,7,8-HxCDD	0.04	12	0.48	40	1.6	66	2.64	86	3.44	11	0.44
1,2,3,6,7,8-HxCDD	0.04	17	0.68	34	1.36	90	3.6	148	5.92	11	0.44
1,2,3,7,8,9-HxCDD	0.04	28	1.12	79	3.16	120	4.8	194	7.76	22	0.88
Other HxCDD	0.0004	154	0.062	342	0.137	925	0.37	853	0.34	104	0.042
1,2,3,4,7,8-HxCDF	0.01	74	0.74	336	3.36	218	2.18	654	6.54	95	0.95
1,2,3,6,7,8-HxCDF	0.01	131	1.31	524	5.24	279	2.79	660	6.60	134	1.34
1,2,3,7,8,9-HxCDF	0.01	36	0.36	127	1.27	193	1.93	479	4.79	45	0.45
2,3,4,6,7,8-HxCDF	0.01	5	0.05	54	0.54	70	0.70	124	1.24	20	0.20
Other HxCDF	0.0001	281	0.0281	939	0.0939	635	0.0635	1,686	0.169	280	0.028
1,2,3,4,6,7,8-HpCDD	0.001	159	0.159	319	0.319	1,849	1.85	1,555	1.56	122	0.122
Other HpCDD	0.00001	140	0.0014	288	0.0028	1,511	0.0151	1,384	0.0138	0	0
1,2,3,4,6,7,8-HpCDF	0.001	129	0.129	539	0.539	653	0.653	1,842	1.84	155	0.155
1,2,3,4,7,8,9-HpCDF	0.001	8	0.008	48	0.048	83	0.083	119	0.119	16	0.016
Other HpCDF	0.00001	51	0.00051	197	0.00197	254	0.00254	384	0.00384	44	0.00044
OCDD	0	313	0	544	0	6,906	0	4,519	0	294	0
OCDF	0	66	0	243	0	563	0	893	0	59	0
TOTAL TEs			74.5		211		119		189		63.7

(1) Toxicity Equivalency Factors are EPA's current recommended Factors, (EPA, March 1987)

ND Not detected below 221 pg/g.

TABLE 4
COMPARISON OF ASH EXTRACT METAL ANALYSES RESULTS
WITH LEACHATE METAL ANALYSES RESULTS

Parameter	Samples (µg/L)							
	EPTOX Extracts	TCLP 1 Extracts	TCLP 2 Extracts	CO ₂ Extracts	DI H ₂ O Extracts	SAR Extracts	Leachate (Literature)(1)	Leachate (CORRE)
Arsenic	ND-31	ND	ND-60	ND-53	ND-45	ND	5-218	ND 400
Barium	23-455	161-1,850	12-809	126-530	ND-3,050	127-3,960	1,000	ND-9,200
Cadmium	25-1,200	ND-1,150	ND-1,560	ND-354	ND-7.6	ND-6.0	ND-44	ND-4
Chromium	ND-86	ND-8.0	ND-799	4.2-9.8	6.8-16	ND-10	6-1,530	ND-32
Copper	24-5,170	5-858	5.4-1,400	8.8-620	12-534	8.5-610	22-24,000	ND-12
Iron	ND-82,000	ND-7,220	ND-162,000	ND-304	ND-115	ND-97	168- 121,000	ND-10,500
Lead	ND-19,700	ND-10,550	ND-26,400	ND-504	ND-3,410	ND-3,940	12-2,920	ND 54
Manganese	250-8,540	ND-5,170	3.8-7,370	ND-2,390	ND-20	ND-6.4	103-4,570	6.7-18,500
Mercury	ND-203	ND-3.8	ND-4.6	ND-155	ND-0.96	ND-1.1	1.8	ND
Selenium	ND	ND	ND	ND	ND	ND-23	2.5-37	ND-340
Silver	ND	ND	ND	ND-16	ND	ND	70	ND
Sodium	33,600- 225,000	1,000,000- 1,640,000	38,700- 228,000	24,800- 168,000	24,100- 209,000	24,200- 201,000	200,000- 4,000,000	14,000- 3,800,000
Zinc	67-95,600	9.7-79,500	26-164,000	5-127,000	5.4-1,340	12-1,290	ND-3,300	5.2-370

TABLE 4
COMPARISON OF ASH EXTRACT METAL ANALYSES RESULTS
WITH LEACHATE METAL ANALYSES RESULTS
PAGE TWO

Parameter	Samples (µg/L)							
	EP TOX Extracts	TCLP 1 Extracts	TCLP 2 Extracts	CO ₂ Extracts	DI H ₂ O Extracts	SAR Extracts	Leachate (Literature)(1)	Leachate (CORRE)
Aluminum Oxide*	ND-150,000	ND-62,800	ND-152,000	ND-90,700	ND-203,000	ND-118,000	NR	ND-920
Calcium Oxide*	592,000- 4,810,000	666,000- 2,750,000	692,000- 3,540,000	398,000- 1,920,000	141,000- 1,740,000	142,000- 1,800,000	21,000	64,600- 8,390,000
Magnesium Oxide*	27,300- 130,000	55-375,000	623-137,000	207-59,300	21-379	12-430	NR	14,800- 367,000
Potassium Monoxide*	10,100- 189,000	14,600- 210,000	15,100- 1,110,00	12,300- 155,000	13,100- 189,000	14,500- 181,000	21,500	10,900- 1,620,000
Silicon Dioxide*	5,090-98,700	379-51,700	820-143,000	418-71,800	402-3,990	364-3,770	NR	ND

ND Not Detected.

NR Not Reported in the literature.

(1) EPA, October 1987.

* The ash extracts were analyzed as ions for these compounds and reported as oxides. The leachates were analyzed and are reported as ions for these compounds.

MOBILITY OF DIOXINS AND FURANS ASSOCIATED WITH STABILIZED INCINERATION
RESIDUES IN THE MARINE ENVIRONMENT

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ABSTRACT

The combustion of municipal solid wastes in "waste to energy" facilities produces ash known to contain trace amounts of organic compounds such as polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Prior investigations have shown that these combustion by-products can be stabilized using Portland cement to form solid concrete-like materials. Small artificial habitats were constructed in Conscience Bay, Long Island Sound, New York using blocks of stabilized incineration residue.

Divers have periodically returned to the site to monitor the interactions of the stabilized incineration ash blocks with the marine environment. Results show that the blocks retain their structural integrity after prolonged seawater exposure. PCDDs and PCDFs were measured in pg/g concentrations and are retained within the cementitious matrix of the block following placement in the sea. Organisms growing on the blocks were found to contain no measurable quantities of organics.

This paper has been reviewed in accordance with U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

In urban coastal areas where landfills are few and increasingly distant, ocean disposal of stabilized incineration residues may provide an acceptable alternative to current landfill practices (1). Previous studies have demonstrated that the stabilization of combustion residues (coal fly ash, oil ash) using additives (lime, sodium carbonate, Portland cement) can be used to produce solid blocks that are environmentally acceptable in the sea (2,3).

In May 1985 a research program was initiated at the Marine Sciences Research Center to examine the feasibility of utilizing stabilized incineration residues for artificial reef construction in the ocean. Results of these studies showed that particulate incineration residues could be combined with cement to form a solid block possessing physical properties necessary for ocean disposal (4). The stabilized residues were subjected to regulatory extraction protocols and in no instance did the metal concentrations in the leachates exceed the regulatory limits for toxicity (5). Bioassays revealed no adverse impacts to the phytoplankton communities exposed to elutriate concentrations higher than could be encountered under normal disposal conditions (4). The success of the laboratory studies resulted in securing the necessary permits for the placement of an artificial habitat constructed using stabilized incineration residue in coastal waters.

April 1987 and again in September 1988, stabilized incineration residue blocks and cement blocks, that serve as a reference material, were submerged in eight meters of water in Conscience Bay, Long Island Sound, New York. The purpose of the September 1988 placement was to confirm the data gathered from the first habitat and examine the fate of PCDD's and PCDF's associated with incineration residue. Divers have periodically returned to the reef site to study the interactions of stabilized incineration residue with the marine environment. Stabilized incineration residue blocks were retrieved from the reef site for physical and chemical testing. Compressive strengths of the reef blocks were measured to monitor the strengths of the blocks and after 13 months of submersion experienced a 5% increase in strength. Samples of blocks exposed to seawater were analyzed for metals to determine if these constituents associated with particulate residues are effectively retained within the stabilized blocks. To date the data suggest that blocks possess concentrations of metals nearly identical to preplacement values supporting the concept that metals are effectively being retained. In addition, divers removed organisms from the surfaces of the blocks to evaluate the possible uptake of metals. No metal enrichment was observed in the tissues of organisms associated with the ash blocks when compared to data collected from organisms removed from concrete control blocks.

The present study was designed to evaluate the mobility of dioxins and furans incorporated in blocks of stabilized incineration ash following placement in the sea.

ASH SAMPLES AND BLOCK PRODUCTION

For the second artificial habitat, placed into the sea in September 1988, incineration residues for block making were collected from the Baltimore Resource Recovery Facility, Baltimore, Maryland in August 1988. Combined ash, a mixture of bottom ash and fly ash, was collected. Prior to block making, the combined ash was sieved to particle sizes less than 3/8". The residue >3/8" was crushed with a jaw-crusher and resieved. Screening the combined ash was necessary to prevent large particles from damaging the block making equipment.

Block manufacturing was conducted in August 1988 at the research facilities of the Besser Company at the Alpena Community College, Alpena, Michigan. Block fabrication employed conventional block making machines currently used by the industry.

REEF PLACEMENT

The "Narrows" region of Conscience Bay, Long Island Sound was selected as the site for the in situ investigations of the interactions of stabilized incineration residues with the marine environment. Conscience Bay is a small embayment immediately west of the Port Jefferson Harbor channel on the northern shore of Long Island. Tidal currents within the "Narrows" can exceed 10 Km/hr (6). As a result, the sediments of Conscience Bay at the reef site are predominantly composed of poorly-sorted gravel and coarse sand. The salinity within Conscience Bay varies between 25.5 to 29.7 ppt and the water temperatures range from 0-24.5°C (5).

Stabilized incineration residue blocks and standard cement blocks were submerged in about 8 meters depth (mean high tide) on September 23, 1988. The blocks were arranged underwater to produce two separate structures, one incineration residue and one cement, approximately 2 meters apart. Each reef was designed to maximize the surface area exposed to seawater and to provide numerous crevices to facilitate biological colonization.

Sample collection on the reef was performed by certified SCUBA divers. Due to strong tidal currents within Conscience Bay, diving activities were restricted to forty-five minutes prior to and after slack water.

ORGANIC EXTRACTION PROTOCOLS

INCINERATION ASH OR STABILIZED INCINERATION RESIDUE

Each sample of incineration ash or coarsely ground stabilized incineration residue is added directly to a glass Soxhlet thimble containing a layer of dichloromethane-extracted silica gel. A finely milled, homogeneous sample is mixed 1:1 with coarse, dichloromethane-extracted, anhydrous sodium sulfate before addition to a glass Soxhlet thimble. The

sample is spiked at approximately 60 pg/g (concentration of each congener) with the $^{13}\text{C}_{12}$ labeled PCDD/PCDF internal standard mixture, covered with a plug of hexane-extracted glass wool, and Soxhlet-extracted with benzene for 16 hours. The extract is concentrated to 25 mL for processing through the following cleanup steps.

BIOMASS

Each sample is added to a 150-mL flask and spiked at approximately 1 ng/g (concentration of each congener) with the $^{13}\text{C}_{12}$ -labeled PCDD/PCDF internal standard mixture. The sample is homogenized with 50 mL of 50% ethanol/cyclohexane using a Virtis Model 45 homogenizer with an UltraShear^R attached. The homogenate is transferred to a 600-mL beaker with three 50% ethanol/cyclohexane rinsings. The suspension is boiled gently for three min. Fifty mL of ethanol and 25 mL of cyclohexane is added and boiling is continued for 20 min. The supernatant is filtered. Fifty mL of 50% ethanol/cyclohexane is added to the biomass remaining in the 600-mL beaker; it is boiled for five min and filtered. The filtered solid is washed two times with 5 mL of cyclohexane, once with 10 mL of ethanol and then the combined washes and filtrates are concentrated to less than 100 mL. The extract is divided between two centrifuge bottles using ethanol rinses. Fifteen mL of cyclohexane and 25 mL of distilled water is added to each. The bottles are centrifuged for five min at 5000 rpm. After the organic layer is removed from each portion, 15 mL of cyclohexane is added, and the centrifugation process is repeated. Another 15 mL of cyclohexane is added to each aqueous layer, and the centrifugation step is repeated. The combined extracts are concentrated to about 2 mL. To remove all the traces of ethanol, another 50 mL of cyclohexane is added, and the extract is again concentrated to about 2 mL and dried over anhydrous sodium sulfate. The extract is dissolved in 25 mL of benzene for processing through the cleanup steps described below.

CLEANUP OF EXTRACTS

The following steps are used to remove interferences from the extracts and enrich the analytes for PCDD/PCDF analysis.

Acid/Base Column

The extract is passed through a mixed acid/base column containing silica gel, sulfuric acid-treated silica gel, and potassium hydroxide treated silica gel with three 10-mL portions of hexane, then 30 mL of hexane. The first 90 mL is collected as the PCDD/PCDF fraction.

Automated Chromatography System

After preliminary cleanup on the acid/base column, the extract is cleaned up using a sequence of acid alumina, carbon, and neutral alumina columns (7). By using the solvent system listed below, the four columns can be used in series with no concentration of the extract. The 90-mL extract

from the acid/base column is applied to the acid alumina column, followed with 30 mL of 3% dichloromethane/hexane and eluted with 70 mL of 50% dichloromethane/hexane onto the carbon column. The 70-mL PCDD/PCDF fraction from the acid alumina column is followed by 50 mL of 10% benzene/hexane in the forward direction. The PCDD/PCDF fraction is eluted with 30 mL of 50% xylene/hexane in the reverse direction onto the neutral alumina column. The 30-mL extract from the carbon column is followed by 37 mL of 3% dichloromethane/hexane, and eluted with 75 mL of 50% dichloromethane/hexane. The extract is concentrated to 100 μ L.

Silica Gel/Micro Diol Column

The concentrated extract from the automated chromatography cleanup is applied to a micro column containing a layer of silica gel and a layer of Bondesil 20H (Analytichem International, Harbor City, CA). The extract is followed by 100 μ L of hexane, then 1.6 mL of hexane. The first 1.6 mL represents the PCDD/PCDF fraction.

Final Sample Concentration

The hexane eluent from the silica gel/micro diol column is concentrated to 100 μ L, replaced with benzene, transferred to a 0.1 mL tapered vial with rinses, and concentrated to about 0.5 μ L. The sides of the vial are washed down with 20 μ L of benzene and the extract is concentrated to about 0.5 μ L. The vial sides are washed down with the recovery standard, $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. The final volume for GC/MS is 4 μ L.

PCDD/PCDF ANALYSIS

The Department of Health Laboratory, in Albany, uses the USEPA Method 8280 "The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans". The system used to analyze a sample extract for the presence of PCDDs and PCDFs is comprised of a Hewlett-Packard (HP) model 5890A Gas Chromatograph (Hewlett-Packard Co., Palo Alto, CA) interface directly to the ion source of an HP 5970B Mass Selective Detector (MSD), and an HP ChemStation. This is a high resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) technique that incorporates an HP 9000 computer (work-station), which controls virtually all instrument parameters and contains the vendor-supplied data-acquisition and processing software.

The HP Ultra 2 fused silica capillary column used separates individual levels of chlorination of PCDDs and PCDFs by retention time into separate windows and effectively separates 2,3,7,8-TCDD from all other TCDD isomers for isomer-specific determination of 2,3,7,8-TCDD.

Data is acquired by selected ion monitoring (SIM). Two ions of the molecular ion isotopic cluster that are characteristic of each tetrachloro through octachloro PCDD or PCDF level of chlorination are monitored. The fragment ions arising from the loss of COCl from the molecular ion are also

monitored. A list of the ions and the respective time intervals in which they are monitored is presented in Table 1.

Software written in this laboratory for the IBM PC and PC-compatibles (8) is used to process the SIM data files. TASQ is a collection of interacting compiled BASIC programs which contain the routines that search the data and follow the decision-making criteria by which PCDDs and PCDFs are found and quantitated using criteria described in USEPA Method 8280.

The mass scale of the MS is calibrated by using perfluorotributylamine (PFTBA). The HP 5970B MSD is autotuned daily to ions at m/z 69, 219, and 502 to meet the isotopic ratio criteria.

RESULTS AND DISCUSSION

The results of the PCDD/PCDF analyses conducted on duplicate samples of the combined incineration ash prior to stabilization is presented in Table 2. All isomers were detected and found in concentrations typical of combined incineration ash (9). The 2,3,7,8-CDDs were detected in increasing concentrations from the lower to the higher chlorination levels in each of the ash samples. TCDD concentrations ranged from 5.3 to 17 pg/g and OCDD from 1100 to 1400 pg/g.

Among the 2,3,7,8 CDFs, the hepta isomer was detected in the highest concentration with a range from 180 to 240 pg/g. The 2,3,4,8-TCDF identified in these analyses represent 2,3,7,8 TCDF and co-eluters. The Ultra 2 GC column used is not isomer specific for 2,3,7,8-TCDF and several other isomers could co-elute at the same retention time. One sample showed no detectable 2,3,7,8 TCDF though we believe it is present. A shifting of the retention time (Table 1) just beyond the retention time tolerance would cause the peak present not to be matched with the standard.

Table 3 presents the PCDD/PCDF concentrations found in stabilized ash blocks prior to and following placement in the sea. Prior to submersion, all 2,3,7,8 isomers were observed in concentrations lower than mean ash concentration reported in Table 2. This is due in part to the addition of 15% Portland cement used as the stabilization additive. Reduction in concentrations beyond that explained by dilution is observed for certain isomers and may be the result of an encapsulation of the ash particles by the cement thereby reducing the extraction efficiency.

Following placement of the blocks in the sea, duplicate analyses indicate no significant reduction of 2,3,7,8-isomers when compared to preplacement results. Milling one sample of the exposed block did result in observing higher concentrations of most 2,3,7,8-isomers. The milled sample had a mean particle size that ranged between 132 μm and 65 μm significantly smaller than the unmilled samples whose particle size ranged between 425 μm and 0.25 inch. Two TCDF isomers were not detected in the milled sample and as explained earlier may be the result of a shifting of the retention time.

Table 4 presents the PCDD/PCDF concentration observed in the hydroid biomass collected from both ash and concrete reference blocks on June 8, 1989, after 258 days of submersion. The only PCDD/PCDF isomer detected above detection limits in the hydroid biomass samples that were removed from both the stabilized ash blocks and concrete control blocks was OCDD. In the biomass sample collected from the concrete blocks, over 1 ng/g of OCDD was detected. It is not unreasonable for OCDD to be detected when no other isomers are observed since it is the most widely dispersed of all the PCDD's and PCDF's in the environment.

The detection limits obtained for the biomass samples were limited by the GC/MS sensitivity. The results do, however, place an upper limit on the amount of PCDD's/PCDF's in the biomass. The higher detection limits obtained may have been caused by the low mass of the samples and/or low recoveries in some samples. In addition, the extraction method used for the biomass samples has been validated for terrestrial samples but not for marine organisms.

CONCLUSIONS

Particulate incineration residues, when combined with Portland cement, can be successfully stabilized into solid blocks using conventional block making technology. The establishment of the Conscience Bay artificial reef site constructed using stabilized incineration residues has provided a unique opportunity to study the *in situ* interactions of stabilized incineration residue blocks with the marine environment. Results of this study, though not reported in this paper, have shown that the stabilized incineration residue blocks have retained their strengths even after prolonged seawater exposure. PCDD's and PCDF's are retained within the cementitious matrix of the stabilized incineration residue blocks after 7 months of submersion. In addition, the organisms growing on the surfaces of the stabilized incineration residue blocks are not accumulating PCDD's or PCDF's from the blocks.

To date, no adverse environmental impacts have been observed at the Conscience Bay reef site due to the presence of stabilized incineration residue blocks. Continued monitoring of the reef site is planned and will provide data to more clearly define the long-term effects of stabilized incineration residue in the marine environment.

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TABLE 1. IONS MONITORED FOR PCDD's AND PCDF's.

Group	Compound	Ions	Time
1	DBF	168.05, 139.05	7.01-18.0 min
	MCDF	202.00, 204.00, 139.05	
	DCDF	236.00, 238.00, 173.00	
	DD	184.00, 155.05	
	MCDD	218.00, 220.00, 155.05	
2	DCDF		18.0-35.0 min
	TrCDF	270.00, 272.00, 209.00	
	TCDF	305.90, 303.90, 242.90	
	DCDD	252.00, 254.00	
	TrCDD	286.00, 288.00	
3	¹³ C ₁₂ -DCDD	264.00, 266.00	35.0-47.0 min
	TCDF		
	PeCDF	339.90, 341.90, 276.90	
	TCDD	321.90, 319.90, 258.90	
	¹³ C ₁₂ -TCDF	317.90, 315.90	
4	¹³ C ₁₂ -TCDD	333.90, 331.90	47.0-60.0 min
	³⁷ C ₁₂ -TCDD	327.90, 262.90	
	PeCDF		
	PeCDD	355.90, 357.90, 292.90	
	¹³ C ₁₂ -PeCDF	351.90, 353.90	
5	¹³ C ₁₂ -PeCDD	367.90, 369.90	60.0-72.0 min
	HxCDF	373.80, 375.80, 312.85	
	HxCDD	389.80, 391.80, 328.90	
	¹³ C ₁₂ -HxCDF	385.85, 387.85	
	¹³ C ₁₂ -HxCDD	401.90, 403.90	
6	HpCDF	407.80, 409.80, 344.80	72.0-82.0 min
	HpCDD	423.80, 425.80, 360.80	
	¹³ C ₁₂ -HpCDF	419.80, 421.80	
	¹³ C ₁₂ -HpCDD	435.80, 437.80	
	OCDF	443.80, 441.70, 378.80	
7	OCDD	459.70, 457.70, 394.80	82.0-95.0 min
	¹³ C ₁₂ -OCDD	455.80, 453.70	
	¹³ C ₁₂ -OCDD	471.80, 469.80	

TABLE 2. PCDD/PCDF CONCENTRATIONS* IN COMBINED INCINERATION ASH

ANALYTE	INCINERATION ASH			
	SAMPLE 1		SAMPLE 2	
	<u>DET. LIMIT</u>	<u>CONC.</u>	<u>DET. LIMIT</u>	<u>CONC.</u>
2378 TCDD	4.7	17	0.38	5.3
12378 PCDD	7.3	19	0.51	17
123678 HXCDD	14	48	1.3	31
123789 HXCDD	12	65	1.1	42
123478 HXCDD	15	26	1.4	17
1234678 HPCDD	20	450	3.2	340
12346789 OCDD	44	1400	18	1100
2378 TCDF	4.2	0	0.32	69
12378 PCDF	5.0	44	0.37	32
23478 PCDF	6.9	54	0.49	17
123478 HXCDF	7.1	80	0.97	39
123678 HXCDF	8.1	57	1.1	66
234678 HXCDF	11	68	1.2	69
123789 HXCDF	11	0	1.1	3.7
1234678 HPCDF	12	240	3.4	180
12346789 OCDF	30	180	12	68

* CONCENTRATIONS EXPRESSED IN pg/g

TABLE 3. PCDD/PCDF CONCENTRATIONS* IN STABILIZED INCINERATION ASH REEF BLOCKS

ANALYTE	STABILIZED INCINERATION ASH BLOCKS									
	REEF BLOCK T=0		REEF BLOCK T=192 SAMPLE 1		REEF BLOCK T=192 SAMPLE 2		REEF BLOCK T=192 MILLED			
	DET. LIMIT	CONC.	DET. LIMIT	CONC.	DET. LIMIT	CONC.	DET. LIMIT	CONC.	DET. LIMIT	CONC.
2378 TCDD	0.6	6.1	0.32	5.5	0.29	4.7	7.0	6.6		
12378 PCDD	0.9	14	0.45	14	0.44	14	13	16		
123678 HXCD	1.7	26	1.2	25	1.7	24	16	30		
123789 HXCD	1.6	34	1.0	37	1.6	42	15	51		
123478 HXCD	1.9	17	1.4	15	1.9	8.9	20	21		
1234678 HPCDD	2.4	230	2.1	270	3.7	240	2.4	230		
12346789 OCDD	6.7	850	6.7	850	18	900	34	1300		
2378 TCDF	0.52	66	0.27	59	0.28	46	6.4	0		
12378 PCDF	0.73	30	0.34	27	0.33	27	7.9	35		
23478 PCDF	0.97	31	0.45	12	0.44	7.9	12	53		
123478 HXCDF	0.95	48	0.83	37	2.7	39	8.8	71		
123678 HXCDF	1.1	34	0.93	57	3.0	79	10	39		
234678 HXCDF	1.2	33	1.1	33	3.5	110	12	49		
123789 HXCDF	1.2	2.4	0.93	3.4	3.3	10	11	0		
1234678 HPCDF	1.7	140	2.4	150	5.8	140	13	180		
12346789 OCDF	4.3	57	4.1	56	12	57	24	76		

* CONCENTRATIONS EXPRESSED IN pg/g

TABLE 4. PCDD/PCDF CONCENTRATIONS* IN HYDROID BIOMASS

ANALYTE	BIOMASS REMOVED FROM CONCRETE BLOCKS			BIOMASS REMOVED FROM INCINERATION ASH BLOCKS		
	SAMPLE 1 DET. LIM	CONC.	SAMPLE 2 DET. LIM	SAMPLE 3 DET. LIM	SAMPLE 1 DET. LIM	SAMPLE 2 DET. LIM
2378 TCDD	17	0	43	43	22	150
12378 PCDD	25	0	93	91	82	230
123678 HxCDD	44	0	150	120	300	360
123789 HxCDD	41	0	140	120	280	330
123478 HxCDD	49	0	180	150	340	420
1234678 HPCDD	100	55	350	270	2500	540
12346789 OCDD	520	1100	1100	620	0	2000
2378 TCDF	17	15	72	81	41	140
12378 PCDF	17	0	25	25	10	140
23478 PCDF	24	0	35	36	14	200
123478 HxCDF	24	0	26	24	25	150
123678 HxCDF	28	0	27	28	28	170
234678 HxCDF	34	0	36	35	33	220
123789 HxCDF	31	0	32	29	31	190
1234678 HPCDF	55	0	39	35	44	250
12346789 OCDF	320	0	100	71	97	840

* CONCENTRATIONS EXPRESSED IN pg/g

WATER MOVEMENT THROUGH AN EXPERIMENTAL SOIL LINER

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ABSTRACT

A field-scale soil liner was constructed to test whether compacted soil barriers in cover and liner systems could be built to meet the U.S. EPA saturated hydraulic conductivity requirement ($\leq 1 \times 10^{-7}$ cm/s). The 8 x 15 x 0.9 m liner was constructed in 15-cm compacted lifts using a 20,037-kg pad-foot compactor and standard engineering practices. Water infiltration into the liner has been monitored for 1 year. Monitoring will continue until water breakthrough at the base of the liner occurs. Estimated saturated hydraulic conductivities were 2.5×10^{-9} , 4.0×10^{-8} , and 5.0×10^{-8} cm/s, based on measurements of water infiltration into the liner by large- and small-ring infiltrometers and a water balance analysis, respectively.

Also investigated in this research effort was the variability of the liner's hydraulic properties and estimates of the transit times for water and tracers. Small variances exhibited by the small-ring flux data suggested that the liner is homogeneous with respect to infiltration fluxes. The predictions of water and tracer breakthrough at the base of the liner ranged from 2.4 to 12.6 years, depending on the method of calculation and assumptions made. The liner appeared to be saturated to a depth between 18 and 33 cm at the end of the first of year of monitoring. Transit time calculations cannot be verified yet, since breakthrough has not occurred. The work conducted so far indicates that compacted soil barriers can be constructed to meet the saturated hydraulic conductivity requirement established by the U.S. EPA.

INTRODUCTION

Despite an increased emphasis on recycling, waste reduction, and waste-to-energy conversion for the alleviation of the waste disposal crisis, land burial of solid wastes will continue to be an integral part of any waste management plan (1). In land burial schemes, compacted soil barriers with low

hydraulic conductivity are commonly used in cover and liner systems to control the movement of liquids and prevent groundwater contamination. Little research has been done to evaluate the effectiveness of field-scale compacted soil barriers in retarding the movement of water and leachates. Soil liners have come under scrutiny by the regulatory and scientific communities because the hydraulic conductivity of these liners has often been greater than expected (2). Although laboratory tests have indicated that liner materials can achieve the hydraulic conductivity required by the U.S. EPA, studies that compared field and laboratory data showed that laboratory measurements can underestimate hydraulic conductivity (3,4,5).

This study was initiated to provide data on the performance of a field-scale soil liner using *in-situ* measurements of construction (e.g., soil density and moisture content) and hydrogeologic parameters (e.g., infiltration rates and moisture movement). This paper summarizes the hydrologic findings from monitoring data collected during the first year of a long-term project involving an experimental liner.

EXPERIMENTAL DESIGN AND METHODS

LINER CONSTRUCTION AND INSTRUMENTATION

The Batestown Till Member of the Wedron Formation, an illitic glacial till, was selected as the material with which to construct an experimental field-scale liner. The selection was based on the physical properties of the till (Table 1) and on preliminary field studies that indicated the till could be compacted such that the saturated hydraulic conductivity was less than 1×10^{-7} cm/s (6,7). Rigid quality control practices were applied during liner construction to ensure uniform moisture content and a maximum clod size less than 15 cm in diameter. The liner measures 8 x 15 x 0.9 m, and was constructed in 15-cm compacted lifts using a 20,037-kg pad-foot compactor and standard engineering practices (8). A shelter was built over the liner to maintain a controlled environment (Figure 1).

The liner was compacted at an average moisture content of 11.5%, 1.5% wet of optimum as determined by the Standard Proctor test. The mean dry density of the liner was 1.84 g/cm^3 , 93% of the maximum Standard Proctor density.

A pond above the liner was filled in April 1988 and is maintained at a depth of 29.5 ± 0.2 cm. Evaporation pans in the pond are used to determine evaporative water loss, a parameter needed for the calculation of a mass water balance for the entire liner. When breakthrough occurs, drainage will be collected in an underdrain system and by pan lysimeters installed beneath each quadrant of the liner.

Four large-ring (1.5-m diameter) and 32 small-ring (28-cm diameter) infiltrometers are used to monitor water infiltration into the liner.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF THE BATESTOWN TILL

K_s (laboratory)					
recompacted		$5.1 \times 10^{-9} \pm 1.0 \times 10^{-9}$	cm/s		
K_s (field)					
prototype		3.6×10^{-8}	cm/s		
Standard Proctor Compaction				Atterberg Limits	
Max. Dry Density	1.98 ± 0.00	g/cm ³		Liquid Limit	$23.3 \pm 0.5\%$
Opt. Moisture Content	$9.9 \pm 0.4\%$			Plastic Limit	$13.1 \pm 1.1\%$
				Plastic Index	$10.1 \pm 1.2\%$
Particle-Size Distribution				Clay Mineral Composition	
Clay	$28.9 \pm 2.8\%$	(< 4 μ m)		Illite	$63.7 \pm 0.6\%$
Silt	$33.4 \pm 2.5\%$	(>4 μ m to <63 μ m)		Chlorite	$9.7 \pm 0.6\%$
Sand	$32.0 \pm 1.2\%$	(>63 μ m to <2mm)		Expandables	$26.6 \pm 0.6\%$
Gravel	$5.8 \pm 2.1\%$	(>2mm)			
Specific Gravity	2.74 ± 0.01	g/cm ³			

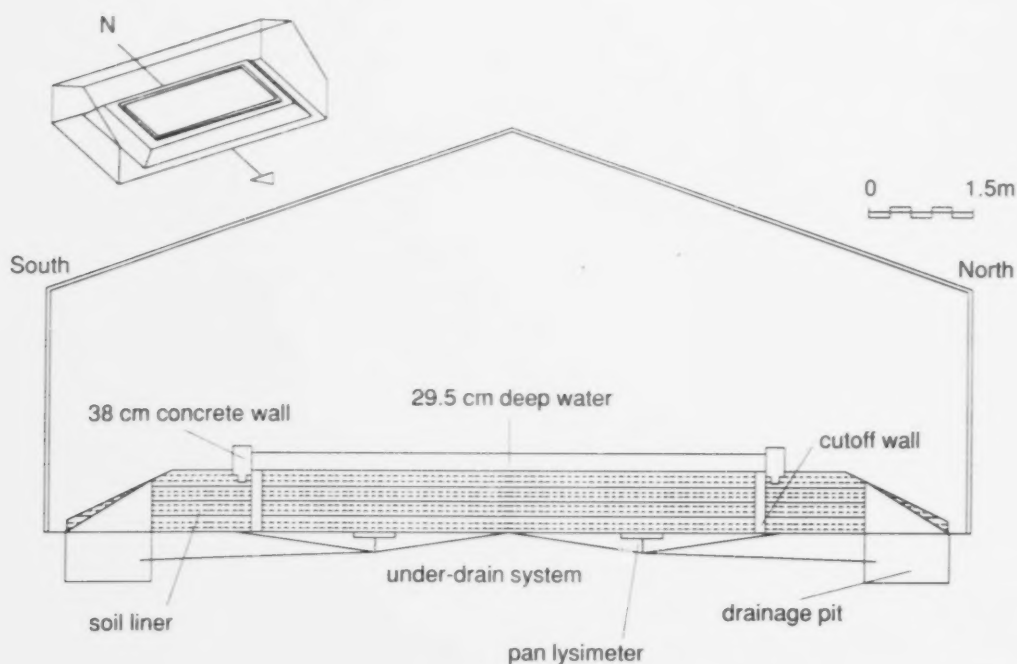


Figure 1. Cross section of the compacted soil liner, shelter, and accessory components.

Tracers (bromide, *o*-trifluoromethylbenzoic acid, *m*-trifluoromethylbenzoic acid, or pentafluorobenzoic acid) were added to the large-ring infiltrometers. Pressure head is monitored using tensiometers installed in 10 nests of six instruments per nest. Each instrument within a nest is located at a different depth in the liner. Samples of soil water are collected using suction cup lysimeters located in 10 nests of six lysimeters (Figure 2). Gypsum blocks were installed in the liner but did not function properly because the liner matric potential was below the working range of the instruments. Further details on liner construction and instrumentation can be found in Krapac et al. (8).

DATA ANALYSIS

Cumulative infiltration curves for each infiltration ring were used to determine steady-state infiltrability; cumulative infiltration volume was plotted and regressed with respect to time since the liner pond was filled (Figure 3). The slope of the linear regression divided by the cross-sectional area of the infiltrometer represented the "average" steady infiltration flux for a 1-year period. The saturated hydraulic conductivity was calculated from the infiltration flux and measured hydraulic gradient.

A vertical hydraulic gradient for each month since the liner pond was filled was calculated from tensiometer data. Monthly gradients were calculated by plotting head at six different depths in the liner against elevation. The data were then analyzed using linear regression; the slope of the regression line represented the hydraulic gradient for the entire liner.

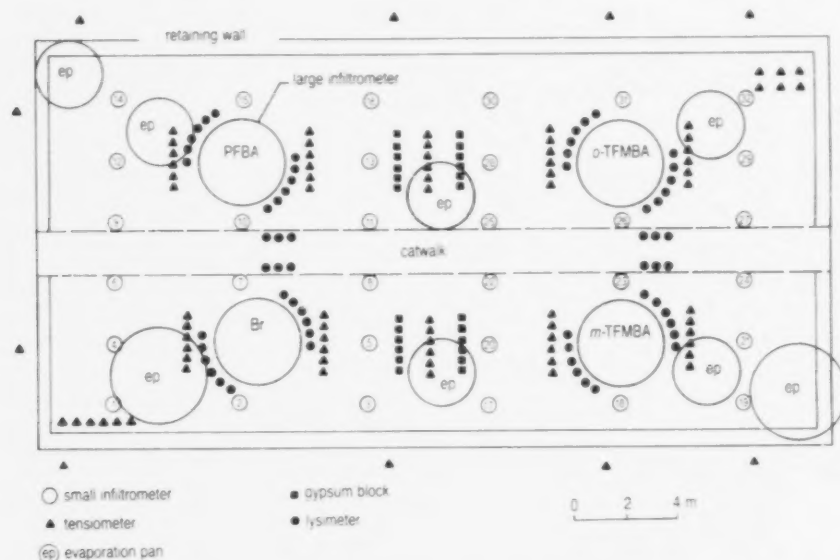


Figure 2. Instrumentation design of the soil liner.

Analytical and numerical methods were used to predict breakthrough times of water and tracers at the base of the liner. The saturated hydraulic conductivity of the liner was also estimated using these methods.

RESULTS AND DISCUSSION

GRADIENTS AND INFILTRATION

The monthly hydraulic gradients ranged from a low of 1.05 in August 1988 to a high of 1.72 in April 1989 with a mean of 1.5 (Figure 3). When the liner reaches steady state, the overall gradient based on the depth of the pond and thickness of the liner will be approximately 1.3. The variation in gradient was related to head changes at various depths in the liner. These head changes were a reflection of soil tension deviations in the liner resulting from long-term atmospheric pressure and temperature fluctuations.

Changes in atmospheric pressure can affect soil pore-water pressure when some of the pore space is occupied by air, a situation likely in the liner. An increase in atmospheric pressure can compress entrapped air, and a pressure decrease can allow entrapped air to expand and occupy more pore space (9, 10, 11). A decrease in air volume, caused by increased atmospheric pressure, would increase tension. This effect may be more apparent in fine-grained materials (11).

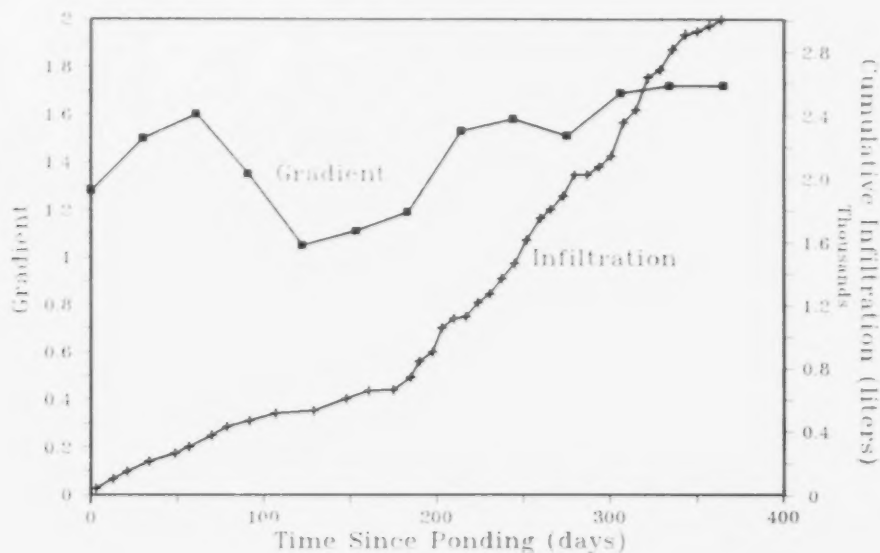


Figure 3. Hydraulic gradients in the liner and cumulative infiltration from April 1988 to April 1989 as determined by pressure transducer tensiometers and a water balance analysis.

A positive relationship has been shown between temperature change and pressure head in soil systems (12, 13), and was observed in this study. Turk (11) suggested that temperature changes have two long-term effects on soil moisture: (1) surface tension is affected in the capillary pores near the soil surface, resulting in drainage of pores when temperature increases; (2) entrapped air can expand or contract—an increased temperature decreases tension.

The average infiltration fluxes were 7.9×10^{-8} cm/s and 5.0×10^{-9} cm/s for the small-ring (SR) and large-ring (LR) infiltrometers, respectively. The infiltration fluxes of the 32 small-ring infiltrometers exhibited a low variance (coefficient of variation = 2%), suggesting a relatively homogeneous distribution of the infiltration rate throughout the liner. The mean fluxes of the two infiltrometer data sets were statistically different at a 99% confidence level, as determined by a t-test. The reason for the difference between these two data sets is not known.

Indirect evidence suggested several likely reasons for the lower infiltration rates of the large rings: (1) water leaked between the grout-soil interface, (2) the measurement capabilities were exceeded by the low hydraulic conductivity of the liner material, and (3) colonies of anaerobic bacteria could have formed mats on the liner surface inside the rings, reducing the permeability of the liner surface.

A mass water balance for the 1-year period was used to determine the overall flux of the liner. During this period, 9860 liters of water was added to the liner pond, and 6600 liters of water was estimated to have evaporated. An estimated 3260 liters of water infiltrated into the liner. After the area of infiltration was corrected to account for the infiltrometers, the average flux for the entire liner was 1.0×10^{-7} cm/s.

HYDRAULIC CONDUCTIVITY ESTIMATES

Darcy's law, the Green and Ampt infiltration approximation (14), and the numerical model SOILINER (15) were used to calculate the saturated hydraulic conductivity of the liner. The three methods produced comparable results with all conductivity values less than the U.S. EPA requirement of 1×10^{-7} cm/s (Table 2).

The application of Darcy's law requires the assumption that all flow through the liner is saturated. Darcy's law can be written as $V = -K I$, where V is the specific discharge, K is the saturated hydraulic conductivity, and I is the hydraulic gradient. Solving for K produces $K = -V/I$; $-V$ is the measured steady-state infiltration flux. The average gradient for the liner after the first year of monitoring as determined from the tensiometer data was 1.5. Hydraulic conductivity values for the liner were calculated from three sets of infiltration data (Table 2).

TABLE 2. HYDRAULIC CONDUCTIVITY VALUES DETERMINED FROM INFILTRATION DATA

Data set	Infiltration flux (cm/s)	Hydraulic Conductivity (cm/s)		
		Darcy's law	Green-Ampt	SOILINER
Small rings	7.9×10^{-8}	5.3×10^{-8}	4.0×10^{-8}	5.7×10^{-8}
Large rings	5.0×10^{-9}	3.3×10^{-9}	2.5×10^{-9}	3.5×10^{-9}
Water balance	1.0×10^{-7}	6.7×10^{-8}	5.0×10^{-8}	7.2×10^{-8}

The Green and Ampt (14) soil infiltrability approximation differs from Darcy's law in that of the depth of the wetting front must be known to estimate a hydraulic conductivity. This approximation technique assumes that the wetting front is uniform and sharp, and has a constant matric potential. The wetted zone is also assumed to have a uniform moisture content and a constant hydraulic conductivity. On the basis of these assumptions, the analytical solution to vertical infiltration is

$$K = i \left[1 + \frac{h + \psi_f}{L_f} \right]^{-1} \quad [1]$$

where the bracketed term is the hydraulic gradient, h is the ponding depth (29.5 cm), ψ_f is the tension at the wetting front (conservatively estimated to be zero), L_f is the depth to the wetting front, and i is the steady-state infiltration flux. Tensiometer data suggested that the wetting front after 1 year of ponding was at a depth between 18 and 33 cm. Table 2 shows the saturated hydraulic conductivities based on the Green and Ampt assumption for the same three data sets used in the Darcy approximation (wetting front depth conservatively estimated to be 30 cm). The conductivity values calculated from Darcy's law were approximately 33% higher than those calculated by the Green and Ampt method because the gradient term increased from 1.5 (Darcy estimate) to approximately 2 (Green-Ampt estimate).

SOILINER estimated a saturated hydraulic conductivity by determining the required model input conductivity that would generate a flux value equal to that measured in the liner. The liner hydraulic gradient was computed by the model based on the head values at the top and bottom of the liner, the soil properties, and the moisture characteristic curve of the compacted liner soil. For example, a flux of 7.9×10^{-8} cm/s, as determined by the small-ring infiltrometers, required the modeled soil column (liner) to have a hydraulic conductivity of 5.7×10^{-8} cm/s (Table 2).

TRACER TRANSIT TIME PREDICTIONS

An objective of this project is to determine the accuracy of transit time predictive methods. Water did not break through at the bottom of the liner during the first year of monitoring, nor have soil-water samples contained detectable concentrations of the tracers. After the first year of monitoring, the predictions cannot be verified, only compared.

The simple and modified transit time equations are analytical solutions used to estimate the earliest breakthrough of tracers at the bottom of the experimental soil liner (5). The numerical models SOILINER (15) and CHEMFLO (16) were also used to estimate tracer breakthrough times. The conductivity value (7.2×10^{-8} cm/s) used in the predictions was the highest value estimated by the infiltration data sets (Table 2). The effective porosity was assumed to equal the total porosity as suggested by the U.S. EPA (5). The porosity (η) was calculated to be 0.33 using the average liner density (1.84 g/cm³) and a particle density of 2.74 g/cm³.

The simple transit time equation assumes that the liner has always been saturated and drains freely at the bottom, that there is steady-state one-dimensional flow, and that dispersion and adsorption are neglected. Transit time was calculated as

$$t = \frac{\eta d}{v} = \frac{\eta d}{K_{sat}} \frac{d}{(h+d)} \quad [2]$$

where d is the liner thickness (90 cm), h is the depth of the liner pond (29.5 cm), v is the Darcian velocity, and all other parameters are as defined above. On the basis of this equation, tracer transit time through the liner was predicted to be 9.9 years.

The modified transit time equation (17) includes suction potential at the bottom of the liner, recognizing that the liner is not in a completely saturated condition. All other assumptions of the simplified transit time equation remain the same. Modifying equation [2] yields

$$t = \frac{\eta d}{v} = \frac{\eta d}{K_{sat}} \frac{d}{(h+\psi+d)} \quad [3]$$

where ψ is suction potential at the bottom of the liner (55 cm, per tensiometer data). The modified transit time method estimated tracer breakthrough in approximately 6.7 years.

SOILINER predicted the transit time of a non-adsorbed, non-diffused, non-dispersed particle from the top of the liner to the base. With input data representative of the field-scale liner, a transit time of 12.6 years was obtained. As with the preceding transit time equations, total rather than effective porosity was used.

CHEMFLO was used to simulate the effects of dispersion and diffusion on the transit time of a non-retarded particle. With dispersion values of 9.0 to 0.2 cm and typical diffusion values for clayey materials (10^{-6} to 10^{-7} cm²/s; 18), transit times of 2.5 to 4.6 years were obtained.

WATER BREAKTHROUGH TIME PREDICTION

The Green-Ampt infiltration model assumes piston flow and can predict the time it will take for the wetting front to reach a prescribed depth in the liner. If the wetting front depth is assumed to be at the base of the liner, the model predicts the time of water breakthrough,

$$t = \left(\frac{\theta_s - \theta_i}{K_{sat}} \right) [L_f - (h + \psi_i) \ln \left(1 + \frac{L_f}{h + \psi_i} \right)] \quad [4]$$

All parameters are defined above, except that L_f (the depth to the wetting front at breakthrough) equals the liner thickness, 90 cm. ψ_i is 7 cm, based on tensiometer data just below the wetting front, and θ_i is 0.21. A breakthrough estimate of 2.4 years produced by using the largest hydraulic conductivity from all the data sets represents the earliest time in which water will exit the bottom of the liner. The use of the Green-Ampt estimated hydraulic conductivity for the entire liner (5.0×10^{-8} cm/s) produced a breakthrough estimate of 3.4 years.

The tensiometer data suggested that the wetting front was at a depth of about 30 cm after a year of ponding. The tensiometer data reflect the actual liner performance and suggest that water should break through in approximately 3 years if the rate of water movement in the liner is assumed to be constant with respect to time. The Green-Ampt breakthrough estimates of 2.4 to 3.4 years for the wetting front to reach the bottom of the liner appears to be consistent with actual data.

SUMMARY AND CONCLUSIONS

On the basis of 1 year of monitoring data, soil liners probably can be constructed to meet the saturated hydraulic conductivity requirement established by the U.S. EPA. Rigid quality control practices will have to be followed during construction if soil liners are to achieve performance specifications. Estimates of the saturated hydraulic conductivity of the liner using either Darcy's law or the Green-Ampt infiltration model and the small-ring infiltration data ranged from 2.5×10^{-9} to 6.7×10^{-8} cm/s. The numerical model SOILINER estimated a saturated hydraulic conductivity of 5.7×10^{-8} cm/s based on measured fluxes; this value differs less than one order of magnitude from those conductivities derived from either the small-ring infiltrometers or mass water balance approach. The infiltration data from the

large- and small-ring infiltrometers suggest that infiltration fluxes were relatively homogeneous throughout the liner; however, the large-ring infiltrometers had significantly smaller infiltration fluxes than did the small-ring infiltrometers.

transit time predictions based on two analytical methods and one numerical method indicated that a non-dispersed, non-diffused tracer will exit the bottom of the soil liner between 6.7 and 12.6 years after ponding. If diffusion and dispersion were taken into consideration, tracer breakthrough could occur in 2.5 to 4.6 years. According to tensiometer data, water breakthrough should occur in approximately 3 years. During the first year of monitoring soil water in the liner no tracers have been detected, and no water has been collected at the bottom of the liner; therefore these predictions cannot be verified.

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HAZARDOUS AND TOXIC WASTES ASSOCIATED WITH URBAN STORMWATER RUNOFF

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ABSTRACT

This paper summarizes some of the information obtained during a research project sponsored and directed by the EPA's Storm and Combined Sewer Research Program and conducted under a subcontract from Foster-Wheeler/Enviresponse. The research project examined a variety of organic and metallic toxicants in stormwater and combined sewer overflow (SCSO) source flows (Pitt and Barron 1990). The study was designed to use rain events and sample locations to illustrate the variables associated with toxicant concentrations in urban runoff. An attempt was made to specifically address the following questions:

1. What are the typical toxicant contaminant levels in stormwater?
2. What are the origins of these toxicants in stormwater?
3. What rain or land use factors affect toxicant concentrations in stormwater?

INTRODUCTION

Stormwater runoff has been identified as a major contributor to the degradation of many urban streams and rivers (Field and Turkeltaub 1981, Pitt and Bozeman 1982, Pitt and Bissonnette 1984). Organic and metallic toxicants are expected to be responsible for much of these detrimental effects, and have been found in urban runoff discharges during many previous studies (EPA 1983; Hoffman, et al. 1984; Fam, et al. 1987; Pereira, et al. 1988).

Table 1 summarizes the estimated discharges of commonly detected organic and metallic toxicants from all U.S. cities having populations greater than 100,000 population (which total about 15,000 square miles, Dept. of Commerce 1980). These cities will be required to participate in the EPA's stormwater permit program (Federal Register, December 7, 1988). These values are for discharges that are directly entering the nation's surface receiving waters. This information is based on the Nationwide Urban Runoff Program (NURP) results of about 100 stormwater outfall samples (EPA 1983). This NURP data is mostly for residential areas, with some commercial area influences. More recent information indicates that industrial stormwater discharges can have many times the concentrations of the toxicants as the areas represented in the NURP data (Pitt and McLean 1986). In addition, base flows occurring in storm drains during dry weather that may be contaminated by non-stormwater discharges (such as industrial waste cross-connections), can also significantly increase these estimated loadings (Pitt, et al. 1990). Therefore, the large discharges noted in Table 1 can be expected to be even much larger, when all urban areas, land uses, and flow regimes are considered. Most importantly, these are actual discharges as monitored at outfalls, and not estimated discharges associated with chemical storage or disposal operations.

METHODOLOGY

This research included the collection and analysis of several hundred urban runoff samples from a variety of source areas and under different rain conditions. A number of combined sewer overflow and detention pond samples were also included in the evaluation portion of these first phase activities. This effort was significantly greater than has been attempted previously for toxic pollutants in stormwater and will enable several critical questions to be addressed, as stated previously in the objectives.

Samples were analyzed for many organic pollutants using gas chromatographs with a mass selective detector (GC/MSD) and with an electron capture detector (GC/ECD) and metals using a graphite furnace equipped atomic adsorption spectrophotometer (GFAA). All samples were also analyzed for particle distributions from about 1 to 100 microns. All samples were also analyzed using a toxicity screening technique. All SCSO samples were also filtered to determine the liquid/solid partition coefficients of the pollutants and the relative toxicities of the filterable and nonfilterable portions of the samples. The following paragraphs briefly summarize the sampling and analyses features of this first phase research effort.

Sampling Effort

About 300 subsamples were analyzed for organic and metallic toxicants, toxicity screening, and particle size distributions. All of these samples were partitioned into filterable and non-filterable components for complete analyses.

The relative importance of different source areas (such as roofs, streets, parking areas, etc.) in contributing toxicants were examined from field studies conducted as part of this research. Samples were collected from the most significant potential source areas in residential, commercial, and industrial land uses. The areas that received the most sampling attention were parking and storage areas in industrial and commercial areas. These areas have been noted in previous studies to have the largest potential of discharging toxicants (Pitt and McLean 1986).

Sheetflow samples were collected during five Birmingham Alabama rains. Replicate samples from many of the same source areas, but during different rains, enabled differences due to rain conditions versus site locations to be statistically evaluated.

Source Area Runoff Grab Samples

The sheetflow samples were collected using manual grab procedures. Hand operated pumps created a vacuum in the sample bottle which then drew the sample directly into the container through Teflon tubes. About one liter of sample was collected, split into two containers: one 500-mL glass with Teflon lined lid was used for the organic and toxicity analyses, and another 500-mL polyethylene bottle was used for the metal and other analyses.

Most of the source area sheetflow samples were obtained from the Birmingham, Alabama area during the first phase of this project. However, cooperative researchers in Seattle, Washington also submitted a limited number of additional stormwater samples for comparison.

CSO Grab Samples

Twenty combined sewer overflow (CSO) outfall grab samples were collected in the New York City area for complete analyses. These outfall samples were used to

make a preliminary evaluation of the relative toxicities of CSOs and urban stormwater runoff. These samples were collected during four different rains in New York.

Organic Pollutant Analyses

The samples were analyzed using a Hewlett Packard 5890 gas chromatograph with a 5970B mass selective detector (GC/MSD), and a Perkin-Elmer Sigma 300 gas chromatograph with an electron capture detector (GC/ECD). The following lists the organic toxicants that were analyzed in these samples:

Pesticides (detection limit: 0.3 ug/L):

BHC, heptachlor, aldrin, heptachlor epoxide, endosulfan, DDE, DDD, DDT, endrin, and chlordane.

Phthalate Esters (detection limit: 0.5 ug/L):

Bis(2-ethylhexyl) phthalate, butyl benzyl phthalate, di-n-butyl phthalate, diethyl phthalate, dimethyl phthalate, and di-n-octyl phthalate.

Polynuclear Aromatic Hydrocarbons (detection limit: 0.5 ug/L):

Acenaphthene, acenaphthylene, anthracene, benzo (a) anthracene, benzo (a) pyrene, benzo (b) fluoranthene, benzo (ghi) perylene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene, fluoranthene, fluorene, indeno (1,2,3-cd) pyrene, naphthalene, phenanthrene, and pyrene.

In addition, selected nitroaromatics, haloethers, and other chlorinated hydrocarbons were also analyzed.

Metallic Pollutant Analyses

The samples were analyzed using a Perkin-Elmer graphite furnace atomic absorption spectrophotometer (GFAA). Standard EPA approved methods were used in these analyses. Aluminum, cadmium, chromium, copper, lead, nickel, and zinc were analyzed in all samples. The detection limits were about 1 ug/L, except for cadmium which had a detection limit of about 0.1 ug/L.

Low detection limits were necessary for these metal analyses. In prior studies, the total forms of most of the metals were well within the detection limits of standard flame atomic absorption spectrophotometer (AAS) procedures, but the filterable portions were commonly not detected (Pitt and McLean 1986; EPA 1983). The partitioning of the heavy metals between the solid and liquid phases is an important factor in determining the treatability of these pollutants and was therefore an important goal of this research. This information is needed to assess the fates of the metals in receiving waters and in treatment processes.

Toxicity Screening Tests

A number of previous studies have found high concentrations of toxic pollutants in SCSOs. Some urban stormwater runoff studies attempted to use conventional 96-hr fish bioassay toxicity tests (such as Pitt 1979), but very few fish died during the tests. However, in situ taxonomic studies of urban runoff receiving waters found significant evidence of toxic effects from the long-term exposure to these pollutants (such as

reported by Pitt and Bozeman 1982, for the same stream as the negative fish bioassay tests). More recent bioassay tests have used more sensitive organisms and have detected significant SCSO toxicities (Spiegel et al. 1984 in Syracuse, NY; Mount et al. 1985 in Birmingham, AL; Mount et al. 1986 in Waterbury, CN; and Norberg-King et al. 1988 in San Francisco Bay).

The objective of this task was to obtain toxicity measurements from a large number of SCSO and source area samples, along with toxicity measurements corresponding to different SCSO sample partitions. It was necessary to use a rapid screening method to examine the relative toxicities for the different samples because of the time and financial limitations of this first phase of the research program. A series of special tests were made to compare toxicities of selected sheetflow and CSO samples to both the screening method and conventional bioassay methods.

The toxicity testing procedure that was used (Microtox from Microbics, Inc.) uses luminescent bacteria to indicate relative toxicities of samples. This procedure was used to screen all of the samples collected during this project. The partitioned samples (filterable and non-filterable for each sample) were all tested for relative toxicity. These data enabled toxicity comparisons between different source areas, in addition to toxicity reduction potential for different treatment processes, to be made. These tests were not used to determine the absolute toxicities of the samples, but only to examine the toxicity differences between the different source areas and sample partitions. In addition, about twenty samples were also analyzed concurrently using a variety of conventional bioassay techniques, for comparison with the Microtox procedure.

Particle Size Analyses

Many SCSO treatment processes are very sensitive to the particle size distributions and settling velocities of the solids (Dalrymple et al. 1975). Wet detention ponds, catchbasins, grass filters, street cleaning, microscreening, filtration, swirl concentrators are some of the treatment methods that require a knowledge of particle size and/or settling characteristics. Additionally, the fate of many toxic pollutants in receiving waters is also very sensitive to these particle physical characteristics. Without knowing the specific particle size distributions and settling velocities, the necessary design information for these controls therefore remains unknown.

Unfortunately, there are wide variations in the particle distributions for different source areas (Pitt and McLean 1986), which makes the design of runoff controls having consistent performance difficult. The objective of this subtask was to obtain a statistically significant number of individual particle size distributions from many SCSO source areas.

A laser particle counter (SPC-510 from Spectrex Corp.) was used to analyze particle size distributions for all of the SCSO and receiving water samples. This instrument produces particle size distribution plots for particle sizes ranging from 0.5 microns to more than 100 microns. Settling column tests are currently being conducted to determine the specific gravities of SCSO samples which will enable settling velocities to be calculated.

Treatability Tests

This project also included tests to examine the treatability of source area and outfall samples. Filtration tests, in conjunction with literature information, enabled an examination to be made of the benefits of typical treatment processes to reduce toxicity and potential toxic pollutant components of SCSOs. This subtask stressed the fate mechanisms (partitioning) that can be later related to specific control processes. As an example, knowing the filterable fraction of the aggregate toxicity of a sample will allow estimates to be made concerning the maximum treatability of the waste by particle

separation processes (such as catchbasins, grass filter strips, and wet detention ponds). The detailed particle size distributions obtained in this research will enable the relative benefits of various sediment barrier practices (such as filtration and screening) to be estimated. Many detailed bench-scale unit processes will be performed during the current phase of this study, and future work will include pilot- and full-scale tests of various treatment practices.

DATA OBSERVATIONS

Toxicity Observations

The Microtox procedure allowed toxicity screening tests to be conducted on each sample's total and filtered components. This screening procedure enabled about 300 samples to be evaluated. The Microtox procedure was not used to determine the absolute toxicity of the samples, or to show that urban stormwater runoff components were in fact toxic. The objectives of these analyses were to identify the most toxic source areas and to identify the approximate toxic reductions possible by complete separation of the unfiltered pollutants from the mixtures.

Actual urban stormwater runoff problems that have been monitored are quite varied, but are probably mostly associated with long-term pollutant exposures, especially through heavily polluted sediments. Receiving water concentrations during runoff events and typical laboratory bioassay tests have not shown many significant short-term receiving water problems (Field and Pitt 1990).

Each sample was tested as unfiltered and filtered. A Millipore 0.45-micron filter was used, under a gentle vacuum, to prepare the filtered samples. The toxicity, as determined by the Microtox procedure, was expressed as three values, I_{10} (the percentage light decrease after about 10 minutes of exposure), I_{35} (the percentage light decrease after about 35 minutes of exposure), and the EC_{50} . The EC_{50} is the sample dilution corresponding to a 50 percent light decrease after a 35 minute exposure. Therefore, only samples that have I_{35} values greater than 50 were further tested to determine the EC_{50} values. Higher values of I_{10} and I_{35} , and lower fractions of EC_{50} , correspond to greater toxicities.

Microbics suggests that light decrease values greater than 60 percent correspond to "highly" toxic samples, light decrease values between 20 and 60 percent correspond to "moderately" toxic samples, and light decrease values less than 20 percent correspond to "not" toxic samples. Table 2 shows the percentages of samples in each category that corresponded to each of these groupings. Also shown on Table 2 are the numbers of samples analyzed in each source area category.

The category having the largest percentage of highly toxic samples was the combined sewer overflows. The urban creeks and detention pond effluents had the largest percentage of samples that can be considered least toxic. The source areas that had the greatest toxic responses were the parking and storage areas.

Tests were conducted on unfiltered and filtered portions of each sample to indicate the toxic reduction potential associated with complete separation of the particulate pollutant components. When the toxic responses of all of the samples were compared, it was found that no significant differences in the toxic responses occurred for the unfiltered versus filtered samples. In many cases, the filtered samples actually indicated greater toxicities than their unfiltered counterparts. This was probably because of normal experimental errors (found to be about 15 percent through controlled testing).

The chemical analyses found that significant portions of the monitored toxicants were associated with the suspended solids (nonfilterable residue). Upon sample filtering, the concentrations of the toxicants were generally greatly reduced. However,

as noted above, the Microtox toxicities of the samples were apparently little affected by filtration. Either other nonmonitored toxicants were responsible for the indicated toxicities and were mostly associated with filterable forms, or the toxicants associated with the suspended solids had little effect on the test organisms. The chemical analyses did find significant portions of the toxicants associated with suspended solids that may form highly toxic sediments in receiving waters. These sediments may adversely affect receiving water beneficial uses long after a runoff event.

In summary, the Microtox analyses indicated short-term toxicities associated with filtered pollutants that would not be removed through sedimentation processes. In contrast, the chemical analyses found significant toxicant concentrations associated with sediment forming materials that would affect long-term toxic responses and these could be partially removed through sedimentation and other particle separation processes.

Suspended Solids Analyses

Suspended solids (particulate residue), turbidity, pH, and particle size distributions were obtained for the unfiltered portions of the samples. The runoff from the paved areas all had relatively low suspended solids concentrations (generally less than 100 mg/L), while some of the sheetflows from unpaved areas had concentrations as high as 750 mg/L. The turbidity values varied in a similar manner; they were all quite low, except for the unpaved areas. Except for roof runoff and storage area runoff, the pH values were within a typical range of about 7 to 8.5. They were as low as 4.4 for roof runoff and as high as 11.6 for storage area runoff. The samples representing complex mixtures of source areas (urban creeks, detention ponds, and CSOs), all had pH values closest to 7.

For any one sample, the particle size distributions were generally narrow; the 10 to 90 percent ranges were represented by particle sizes as close as 20 microns apart. The smallest particle sizes were found for roof runoff. In contrast, landscaped areas and loading docks had some of the largest particle sizes found.

Organic Toxicant Concentration Observations

A major portion of the effort of this research project was spent in conducting the organic toxicant analyses. Table 3 summarizes the organics that were observed in at least ten percent of the unfiltered samples analyzed. Most of the organic compounds detected were PAHs. Two ethers were also frequently detected. This list is similar to the frequency of detection list prepared by the EPA (1983) as part of the Nationwide Urban Runoff Program.

Table 4 contains all of the observed base neutral data, while Table 5 contains all of the observed pesticide data. Roof runoff, urban creeks, and the CSOs had the greatest number of observed maximum organic toxicant values. As noted previously, the CSO category had the largest percentage of highly toxic samples. The roofs contained high concentrations of several pesticides, fluoroanthenes and a pyrene. A CSO sample had an extremely high bis (2-ethyl hexyl) phthalate concentration of 56 mg/L. Vehicle service areas and parking areas also had several of the observed maximums.

Heavy Metal Concentration Observations

Table 6 summarizes the heavy metal observations. In contrast to the organic analyses, the detection frequencies for all of the metals were very high. Roof runoff had the highest concentrations of zinc, probably associated with galvanized metal. Parking areas had the highest nickel concentrations, vehicle service areas had the highest

cadmium and lead concentrations, while streets had high aluminum concentrations. Surprisingly, landscaped areas had the highest chromium and urban creeks had the highest copper concentrations.

Many observations of filterable metals were also made and are also summarized on Table 6. Except for storage areas, most of the zinc was associated with the filterable sample partitions. In contrast, very little of the nickel was found in the filterable sample partitions. Most of other metals were also found associated with the suspended solids fraction. Therefore, suspended solids separation processes would be very effective in removing heavy metals from these source areas, with the exception of zinc. Similarly, if the metals were not removed before discharge, they would likely contribute to polluted sediments in the receiving waters.

CONCLUSIONS

The following paragraphs summarize the major project conclusions, as they related to the project objectives.

Objective 1: Characterization of Toxic Components in SCSOs

Overall, about 300 sample components were analyzed to determine toxicant concentrations in sheetflows and other SCSOs as part of the first phase of this project.

Most pH values were in a narrow range of 7 to 8.5 and the suspended solids concentrations were generally less than 100 mg/L. The particle size ranges were usually narrow for any one sample, but the distribution ranges developed using all samples from a single source area were substantially greater.

Only a small fraction of the toxic organic pollutants analyzed were frequently detected. Thirteen organics were detected in more than ten percent of all samples analyzed. The greatest detection frequencies were for 1,3-dichlorobenzene and fluoranthene, which had detection frequencies of 23 percent. The organics most frequently found in these samples were similar to organics most frequently detected in prior studies conducted elsewhere and were mostly the PAHs, especially fluoranthenes and pyrenes.

Roof runoff, urban creeks, and CSO samples had the greatest frequencies of detection for the organic compounds analyzed. Vehicle service areas and parking areas had several of the observed maximum organic compound concentrations observed. Very little evidence was obtained to differentiate the solid/liquid partitioning of organics for different source areas.

The detection limits of the analyses were greater than anticipated and the frequency of detection was therefore less than if the detection limits were improved. The use of larger sample volumes would have reduced the detection limits, which would result in substantially greater detection frequencies. Most of the organics were associated with unfilterable sample portions. In contrast to the organics, the heavy metals were detected in almost all samples analyzed, including the filtered samples.

Roof runoff had the highest concentrations of zinc observed, probably due to galvanized roof drainage components. Parking areas had the highest nickel concentrations, while vehicle service areas had the highest concentrations of cadmium and lead. Urban creek samples had the highest copper concentrations, probably due to illicit discharges.

Objective 2: Relative Toxicities of Sheetflows and SCSOs

The toxicity and chemical tests were not conducted to demonstrate the toxicity of urban runoff. Many actual receiving water studies (summarized in the project report

Pitt and Barron 1990; and by Field and Pitt 1990) identified the various problems that have been associated with urban stormwater discharges. These long-term receiving water studies have demonstrated that actual urban stormwater problems are quite varied, and are probably mostly associated with long-term exposures to toxicants, especially in the sediments, and to habitat destruction associated with high flows and debris. Receiving water concentrations during runoff events and typical laboratory bioassay tests have not indicated many significant short-term problems associated with urban stormwater runoff.

The Microtox screening tests found that CSOs had the greatest percentage of samples considered the most toxic, followed by samples obtained from parking and storage areas. Runoff from paved areas all had relatively low suspended solids concentrations and turbidities, especially compared to samples obtained from unpaved areas.

About 15 percent of all of the unfiltered samples analyzed were considered highly toxic using the Microtox screening procedure. The remaining samples were approximately evenly split between being moderately toxic and not being toxic.

Preliminary data evaluations indicated that variations in observed Microtox toxicities and organic toxicant concentrations may be greater for different rains than for the different source areas sampled. As an example, high concentrations of PAHs were mostly associated with long-antecedent dry-periods.

Objective 3: Partitioning of Toxic Components and Treatability of Toxicants in SCSOs

There were no significant differences in the measured Microtox toxicities associated with the unfiltered samples and the filtered portions of the samples. However, most of the organics and metals were associated with the suspended solids of the runoff samples. An exception was for zinc, which was found mostly in the filtered sample portions. This implies that most of the Microtox measured toxicity was associated with filterable forms of the pollutants.

This preliminary result suggests that simple sedimentation, even though removing much of the mass of toxic pollutants from the water, may have minimal benefits in reducing immediate toxicant effects. Uncontrolled sedimentation, such as in lakes or reservoirs, or large rivers, may result in long-term contaminated sediment problems. However, controlled sedimentation in SCSO control devices allow effective residue management, including appropriate disposal of the potentially heavily contaminated sediments, which would minimize downstream receiving water sediment problems.

The literature review of the potential transport and fate mechanisms of these pollutants found that many processes will affect these pollutants. Sedimentation in the receiving water is the most common fate mechanism because many of the pollutants investigated are mostly associated with particulate matter. Exceptions included zinc and 1,3-dichlorobenzene which were mostly associated with the filterable sample portions. Particulate removal can occur in many SCSO control processes, including catchbasins, swirl concentrators, screens, drainage systems, and detention ponds. These control processes allow removal of the accumulated polluted sediment for final disposal in an appropriate manner. Uncontrolled sedimentation will occur in receiving waters, such as lakes, reservoirs, or large rivers. In these cases, the wide dispersal of the contaminated sediment is difficult to remove and can cause significant detrimental effects. Biological or chemical degradation of the toxicants in the sediments may occur, but is quite slow for many of the pollutants in the expected anaerobic environments. Degradation of the soluble pollutants in the water column may occur, especially when near the surface in aerated waters. Volatilization (evaporation) is also a mechanism that may affect many of the detected organic toxicants. Increased turbulence and oxygen supplies would encourage these processes that may significantly reduce pollutant concentrations.

Sorption of pollutants onto solids and metal precipitation increases the sedimentation potential of the pollutants and also encourages more efficient bonding of the pollutants in soils, preventing their leaching to surrounding waters.

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Table 1. Estimated Toxicant Discharges from Large U.S. Municipalities (15,000 square miles total)

	Median Conc. (ug/L)	Detection Frequency (%)	Discharges (tons/year)
Arsenic	7	50	80
Chromium	30	60	350
Copper	35	90	700
Cyanide	40	25	200
Lead	150	95	3000
Zinc	150	95	3000
Bis(2-ethylhexyl) phthalate	6	20	30
Chlordane	1.5	20	5
Chrysene	1.5	10	3
Fluoranthene	3	15	10
Pentachlorophenol	15	20	70
Phenanthrene	1.5	10	4
Pyrene	2	15	8

Source: from EPA 1983

Table 2. General Toxicity Groupings of Analyzed Samples

	most toxic	moderately toxic	least toxic	number analyzed
roofs	8%	58%	33%	12
parking areas	19	38	44	16
storage areas	25	50	25	8
streets	0	67	33	6
loading docks	0	67	33	3
vehicle service areas	0	40	60	5
landscaped areas	17	33	50	6
urban creeks	0	12	88	19
detention ponds	10	10	80	12
CSOs	65	30	5	20

Table 3. Detection Frequencies of the Most Frequently Occurring Organic Compounds

Frequency of detection:

1,3-Dichlorobenzene	23%
Fluoranthene	23
Pyrene	19
Benzo (b) fluoranthene	17
Benzo (k) fluoranthene	17
Benzo (a) pyrene	17
Bis (2-chloroethyl) ether	14
Bis (chloroisopropyl) ether	14
Naphthalene	13
Chlordane	13
Benzo (a) anthracene	12
Benzyl butyl phthalate	12
Phenanthrene	10

Table 4. Observed Base Neutral Compounds ($\mu\text{g/L}$)

number of nonfiltered analyses:	roof runoff 12	parking 13	storage 7	streets 6	loading dock 3
Base Neutrals					
Bis (2-chloroethyl) ether	20.3;20.5;86.6	15.3; 23.8		15.1	
1,1-Dichlorobenzene	13.6;54.7;88.4	9.6;33.2;60.2	16.2	5.4	
Bis (chloroisopropyl) ether	67.8;81.5;147	81.4;102;217			
Hexachloroethane	55.8	40.9;47.2			
Bis (2-chloroethoxyl) methane	47.7;187	71.8			
Naphthalene					
Acenaphthylene					
Fluorene	31.2	12.8;41			
Di-n-butyl phthalate	22.1				
Phenanthrene	23.7				
Anthracene	105	23.3;21.4			
Benzyl butyl phthalate	7.6;15.3;44.8	1.0;15.6;93.8	4.5	0.6	
Fluoranthene			31.2	305	
Bis (2-ethyl hexyl) phthalate	27.6	1.0;40.2;79.6	8	0.7	
Pyrene	16.3	1.8;16.2;54.8			
Benzo (a) anthracene	73.1	29.3			
Chrysene	6.4;14.2;27.5;266	10;17.5;132		13.9	
Benzo (b) fluoranthene	3.4;11.5;12.2;221	8;11.3;41.6		15.4	
Benzo (k) fluoranthene	10.9;34;51.6;300	21.4;19.5;78.3		18.8	
Benzo (a) pyrene		19.7			
Benzo (g,h,i) perylene					
Di-n-octyl phthalate					
Nitrobenzene					
Isophorone					
Diethyl phthalate					

Table 4. Observed Base Neutral Compounds (µg/L) (cont'd.)

nonfiltered analyses:	vehicle service areas 4	landscaped areas 5	urban creeks 4	detection points 4	New York CSOs 19	overall detection freq. 19	overall maximum
Base Neutrals							
Bis (2-chloroethyl) ether	45.2	56.3	204	15.3	15.5	140	204
1,3-dichlorobenzene	6164.6;72.2	4.5;27.5;54.4	65;120	27	22	23	120
Bis (chloroisopropyl) ether	74;161	85.2	40;78	53		14	217
Hexachloroethane	57		25;38			9	57.3
Bis (2-chloroethoxyl) methane		26;11.5	20.9			4	20.9
Naphthalene	36.7;104	49.4	296	18;68	7.7	13	296
Acenaphthylene	21.9					1	21.9
Fluorene	0.8					3	9.3
Di-n-butyl phthalate	11.2	27.9	68.9	10.4	9.3	3	60.6
Phenanthrene	44.3	20.3	40	5.8	17.1;17.4;18;61	6	68.9
Anthracene		128	58.9	12.9	33.2	10	44.3
Benzyl butyl phthalate	23.8;47.3				82.3	6	128
Fluoranthene	20.4;25.4;52.8	0.7;1.3;38.1	128	6.6;13.9	6.6	23	128
Bis (2-ethyl hexyl) phthalate					115;142;541	9	56,000
Pyrene	20.7;37.7;51	2.3;8.2	102	6;57	836;56,000	19	102
Benzo (a) anthracene	31.1;39	54.1	60.6		15.3	12	60.6
Chrysene	25		237		10.9	6	237
Benzo (b) fluoranthene	89.6;107	29.7	864		8.2	17	266
Benzo (k) fluoranthene	14.7;103	61.4	3178			17	221
Benzo (a) pyrene	59.7;120	54	19;126			17	300
Benzo (g,h,i) perylene						1	19.7
Di-n-octyl phthalate					42.6	1	42.6
Nitrobenzene					26.5	1	26.5
Isophorone					10.4	1	10.4
Diethyl phthalate					103	1	103

Table 5. Observed Pesticides (ug/L)

Number of analyses:		roof runoff	parking	storage	streets	loading dock	vehicle service area	New York CSOs	overall detection frequency	overall maximum
		12	13	7	6	3	4	19		
<u>Pesticides</u>										
alpha BHC	0.7									0.7
delta BHC	1.1									1.1
aldrin	0.7									0.7
DDT	0.3; 46.3		0.3							46.3
endrin			1.4							1.4
chlordane	0.5; 0.9; 2.2		0.8; 1.2	1.1	0.8	1.0	0.8	0.5	13	2.2
DDD								1.2	1	1.2
								all BHCs:	all BHCs:	
								0.3	4%	
									1	
									4	
									1	
									13	
									1	

Table 6. Observed Source Area Metal Concentrations (µg/L)

Source Area Runoff	Aluminum		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.
roofs														
detection frequency	11/12	9/12	11/12	8/12	7/12	2/12	11/12	7/12	12/12	1/12	10/12	0/12	12/12	12/12
median	270	13	0.82	0.23	7	<1	17	1.2	13	<1	5.1	<1	100	83
maximum	8370	1550	30	0.95	510	2.3	900	8.7	170	1.1	70	<1	1580	1550
% filt. (range, median)	2-100	(15%)	1-69	(50%)	6-14	(10%)	4-87	(20%)	7	(<10%)		(<20%)	57-100	(90%)
parking areas														
detection frequency	12/12	10/10	11/12	4/10	11/12	4/12	12/13	9/12	13/13	5/13	11/13	1/13	13/13	13/13
median	1560	360	0.72	<0.1	18	<1	20	1.8	30	<1	40	<1	30	23
maximum	22,500	2890	70	1.0	310	2.4	770	9.2	130	2.5	130	1.6	150	88
% filterable	1-100	(20%)	<1-53	(20%)	2-82	(35%)	<1-40	(15%)	1-45	(10%)		(<5%)	15-100	(75%)
storage areas														
detection frequency	6/6	1/7	7/7	4/7	7/7	4/7	7/7	5/7	7/7	6/7	7/7	0/7	6/6	6/6
median	975	<1	2.4	0.27	60	1.1	30	1.0	30	1.6	30	<1	66	9
maximum	6990	37	10	1.3	340	32	300	1.7	330	5.7	90	<1	290	103
% filterable		(1%)	3-13	(10%)	3-46	(10%)	1-15	(3%)	2-50	(10%)		(<3%)	3-100	(15%)
streets														
detection frequency	4/4	4/4	6/6	5/6	5/6	4/6	6/6	5/6	6/6	4/6	5/6	0/6	5/5	5/5
median	4,000	200	0.76	0.18	3.3	1.3	15	1.9	30	1.3	3.0	<1	58	23
maximum	10,040	4,380	220	0.57	30	2.7	1,450	11.4	150	3.9	70	<1	130	76
% filterable	1-44	(20%)	12-91	(50%)	9-60	(30%)	<1-57	(10%)	4-100	(20%)		(<30%)	8-100	(60%)
loading docks														
detection frequency	3/3	1/3	3/3	3/3	3/3	0/3	3/3	2/3	3/3	1/3	3/3	1/3	2/2	2/2
median	810	<1	1.2	0.5	8.9	<1	20	2.6	60	<1	7.8	<1	55	33
maximum	930	<1	2.4	0.6	40	<1	30	15	80	2.3	8.1	1.3	79	62
% filterable		(<5%)	23-41	(40%)		(<10%)	9-100	(10%)		(<5%)		(<10%)	13-78	(50%)
vehicle service areas														
detection frequency	4/4	3/3	4/4	2/4	4/4	0/4	4/4	3/3	4/4	1/4	4/4	0/4	4/4	4/4
median	920	200	8	<0.2	19	<1	8.3	2.1	75	<1	35	<1	67	18
maximum	1370	410	30	0.34	320	<1	580	6.3	110	1.4	70	<1	130	83
% filterable	<1-87	(30%)	1-16	(<5%)		(<5%)	<1-95	(20%)		(<5%)		(<5%)	10-100	(40%)

Table 6. Observed Source Area Metal Concentrations (μ/L) (cont'd.)

Source Area Runoff	Aluminum		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.	non filt.	filt.
landscaped areas														
detection frequency	4/4	4/4	3/5	1/5	5/15	4/5	4/4	4/4	5/5	1/5	3/5	0/5	5/5	5/5
median	2500	1600	0.04	<0.1	100	1.5	80	2.0	9.4	<1	30	<1	32	32
maximum	4610	1860	1.0	1.0	250	4.1	300	8.3	70	1.7	130	<1	1160	670
% filterable	34-93	(50%)	($<25\%$)		2-68	(10%)	3-20	(3%)	($<10\%$)		($<5\%$)		58-100	(100%)
New York CSOs														
detection frequency	19/19	-	20/20	20/20	20/20	1/20	20/20	16/20	20/20	14/20	20/20	19/20	20/20	20/20
median	720		1.6	0.25	17.6	<1	70	9.1	40	1.6	11.3	5.5	96	34
maximum	23,030		10	5.1	130	18	340	30	120	7.5	48.2	48.2	390	80
% filt. (range, median)			2-100	(35%)	($<5\%$)		2-100	(20%)	2-100	(15%)	12-100	(50%)	3-100	(35%)
urban creeks														
detection frequency	4/4	4/4	4/4	0/4	4/4	0/4	4/4	3/4	4/4	0/4	3/4	0/4	4/4	4/4
median	1600	240	5	<0.1	6.8	<1	160	1.2	38	<1	20	<1	24	19
maximum	3250	500	30	<0.1	30	<1	440	1.4	100	<1	70	<1	32	23
% filterable	13-42	(%)	($<1\%$)		($<15\%$)		<1-23	(20%)	($<3\%$)		($<5\%$)		53-100	(80%)
detention ponds														
detection frequency	4/4	4/4	4/4	1/4	3/4	0/4	4/4	0/4	4/4	0/4	3/4	0/4	4/4	4/4
median	550	200	0.24	<0.1	5.5	<1	47	<1	1.9	<1	20	<1	22	22
maximum	1350	330	1.0	<0.1	230	<1	210	<1	8.8	<1	70	<1	25	25
% filterable	6-100	(60%)	($<5\%$)		($<20\%$)		($<2\%$)		($<25\%$)		($<5\%$)		(all 100%)	

DEGRADATION OF CHLORINATED BIPHENYLS BY ESCHERICHIA COLI CONTAINING CLONED
GENES OF THE PSEUDOMONAS PUTIDA F1 TOLUENE CATABOLIC PATHWAY

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ABSTRACT

Pseudomonas putida F1 initiates the degradation of toluene by a multicomponent enzyme system designated toluene dioxygenase. The enzyme system consists of a flavoprotein (reductase_{TOL}), a ferredoxin (ferredoxin_{TOL}), and an iron-sulfur protein (ISP_{TOL}). Electrons are accepted from NADH by reductase_{TOL} and transferred through ferredoxin_{TOL} to the terminal dioxygenase, ISP_{TOL}. Reduced ISP_{TOL} catalyzes the addition of molecular oxygen to the aromatic nucleus stereospecifically to form cis-dihydrodiols from a variety of aromatic substrates. The cis-dihydrodiols are oxidized to catechols which are the substrates for meta ring cleavage by catechol dioxygenase. Certain bacteria that degrade polychlorinated biphenyls (PCBs) utilize an analogous pathway. Homology studies between PCB degrading strains and P. putida F1 have indicated that the enzymes involved are quite similar. We have constructed strains of Escherichia coli that express the cloned genes of the P. putida F1 toluene catabolic pathway under the control of the tac promoter. These strains were utilized to show that the initial enzymes in the toluene catabolic pathway can also oxidize certain chlorinated biphenyls.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of aryl halides synthesized by the catalytic chlorination of biphenyl. Depending on the number of chlorines and their position on the biphenyl ring structure 209 PCB congeners are possible. They are extremely stable compounds, resistant to acids, bases, and oxidation, possess high dielectric constants, and are highly insoluble in water. Due to these properties, they find extensive use in industry in capacitors, transformers, dielectric fluids, fire retardants, and plasticizers. The very properties which make them extremely useful in industry has also made them very persistent pollutants in the environment. Although PCBs are no longer synthesized, considerable amounts have previously been introduced into the environment where they tend to persist for long periods of time. This is due to the resistance of many individual PCBs to biodegradation. This is particularly true for highly chlorinated PCBs (containing more than 5 chlorines) (1,2). The lipophilic nature of PCBs causes them to concentrate in the food chain. This is of concern to human health particularly since their long term effects are not fully understood.

Several reports have now been published on the study of the biodegradation of PCBs. There is evidence that particular PCBs can undergo microbial reductive dehalogenation in anoxic sediments (3,4). Several reports have also shown that particular PCBs can be degraded aerobically by mixed or pure bacterial cultures. Bedard and coworkers have developed an assay for screening and characterizing bacteria that degrade PCBs ranging from di- to hexachlorobiphenyls (5). Two strains, Alcaligenes eutrophus H850 and Pseudomonas sp. LB400, have shown unique abilities to degrade highly chlorinated PCBs like penta- and hexachlorinated biphenyls in addition to the lower chlorinated biphenyls (5). A 2,3-dioxygenase attack has been reported as the first step in the degradation of PCBs by several strains in addition to A. eutrophus H850 and Pseudomonas sp. LB400 (6,7). Pseudomonas sp. LB400 has been shown to oxidize a wide variety of PCBs and specific intermediates in the degradative pathway have been isolated and identified (8,9). A novel 3,4-dioxygenase attack on 2,5,2',5'-tetrachlorobiphenyl has been reported by Nadim et. al. (8) by both A. eutrophus H850 and Pseudomonas sp. LB400. This observation may be explained by a biphenyl 2,3-dioxygenase with relaxed substrate specificity or by the presence of a second biphenyl dioxygenase which attacks at the 3,4 position (9). The Pseudomonas sp. LB400 genes responsible for the degradation of biphenyl to 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoic acid have been cloned into E. coli. This recombinant strain degrades the same spectrum of PCBs as Pseudomonas sp. LB400 (10).

The initial reactions involved in the oxidation of biphenyl (the aromatic nucleus of PCBs) by Pseudomonas sp. LB400 are shown in Figure 1A. Analogous pathways are utilized in the degradation of a variety of aromatic hydrocarbons (11). Biphenyl is first oxidized to cis-biphenyl dihydrodiol by the action of biphenyl dioxygenase. cis-Biphenyl dihydrodiol is further dehydrogenated to form 2,3-dihydroxybiphenyl. The latter compound

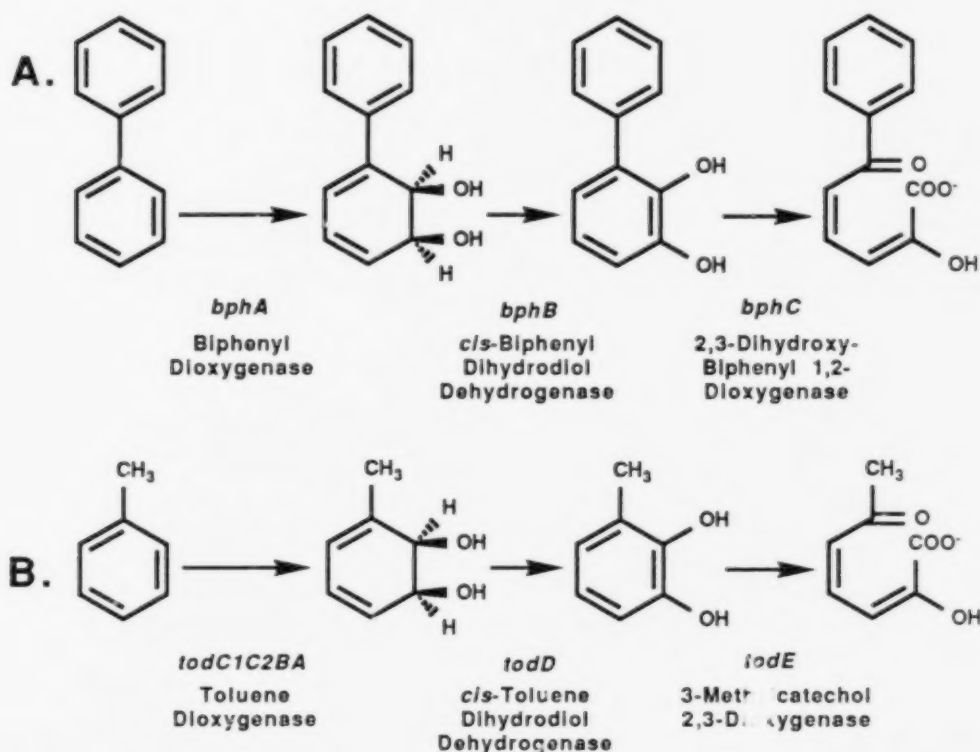


Figure 1. A. Metabolism of biphenyl by *Pseudomonas* sp. 400.
B. Metabolism of toluene by *Pseudomonas putida* Fl.

undergoes ring cleavage by 2,3-dihydroxybiphenyl dioxygenase to form 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoic acid. The genes for these three enzymes have been designated *bphA*, *bphB*, and *bphC*, respectively.

A similar pathway for the degradation of mononuclear aromatic hydrocarbons has been shown in *Pseudomonas putida* Fl (11, Figure 1B). Degradation of toluene (and other compounds) by this microorganism proceeds through a *cis*-dihydrodiol, a 2,3-catechol, and a ring fission product, all of which are structurally similar to intermediates in the pathway for the aerobic degradation of biphenyls. Such similarity also extends to the structural gene sequences encoding for particular proteins in the two degradation pathways. It has been shown previously that the *P. putida* Fl genes for *cis*-toluene dihydrodiol dehydrogenase (*todD*) and 3-methylcatechol dioxygenase (*todE*) share 61% homology at the nucleotide level with the *P. pseudoalcaligenes* KF707 genes for *cis*-biphenyl dihydrodiol dehydrogenase (*bphB*) and 2,3-dihydroxybiphenyl dioxygenase (*bphC*) (12).

In the present work we investigated whether the *P. putida* Fl genes for toluene dioxygenase (*todC1C2BA*), *cis*-toluene dihydrodiol dehydrogenase (*todD*), and 3-methylcatechol 2,3-dioxygenase (*todE*) are homologous to the

analogous *Pseudomonas* sp. LB400 genes for biphenyl dioxygenase (bphA), cis-biphenyl dihydrodiol dehydrogenase (bphB), and 2,3-dihydroxybiphenyl 1,2-dioxygenase (bphC). We also investigated whether such structural homology extended to functional homology by investigating the ability of enzymes in the *P. putida* F1 toluene degradative pathway to metabolize certain PCBs.

MATERIALS AND METHODS

BACTERIAL STRAINS, PLASMIDS, AND MEDIA

P. putida F1 (13) and F39/D (14) have been described previously. *P. putida* F39/D is a todD mutant derived from *P. putida* F1 by N-methyl-N'-nitro-N-nitrosoguanidine mutagenesis. *P. putida* F39/D therefore accumulates cis-diols when incubated with aromatic compounds after induction. *Pseudomonas* sp. LB400, a PCB degrading strain, was previously isolated from PCB-contaminated soil (15). The recombinant plasmid pGEM456 (10) contains the *Pseudomonas* sp. LB400 bphABC genes (responsible for the first three steps in PCB metabolism by this strain) cloned into pUC18. The recombinant plasmid pDTG351 (16,17) contains the *P. putida* F1 todC1C2BADE genes (responsible for the first three steps in toluene metabolism by this strain) cloned into the broad host range vector pKT230. Plasmid pDTG601 and pDTG602 (12) contain the todC1C2BA genes and the todC1C2BAD genes, respectively, cloned into the expression vector pKK223-3 so as to place gene expression under control of the tac promoter. Thus, *E. coli* strains containing either pDTG601 or pDTG602 will accumulate cis-toluene dihydrodiol or 3-methylcatechol, respectively, from toluene after induction with isopropyl- β -D-thiogalactopyranoside. *E. coli* strain JM109 (recA1 endA1 gyrA96 trp1 hsdR17 supE44 relA1 Δ (lac-proAB) [F' traD36 proAB lacI^q ZAM15]) was used as host for plasmids pDTG601 and pDTG602.

Mineral salts base medium (MSB) was prepared as described previously (18). Arginine (0.2%), toluene (vapor phase), or glucose (20 mM) served as carbon sources. Thiamine (1 mM) was added to *E. coli* JM109 cultures. Ampicillin (100 μ g/ml) was added to plasmid-containing cultures to prevent plasmid loss.

DNA TECHNIQUES

Plasmid DNA was prepared by the alkaline-sodium dodecyl sulfate procedure of Birnboim and Doly (19) as described by Ish-Horowitz and Burke (20) and purified by centrifugation in a cesium chloride-ethidium bromide density gradient. DNA was stored in 10 mM Tris 1 mM EDTA (pH 8.0) at -20°C. Plasmid DNA was cleaved with restriction enzymes as recommended by the supplier (Bethesda Research Laboratories, Inc., Gaithersburg, Md.). Agarose gel electrophoresis (1.0%) was conducted in 40 mM Tris, 20 mM acetate, 2 mM EDTA buffer. Transfer of DNA from agarose gels to Zeta-probe nylon membranes (Bio-Rad Laboratories, Rockville Centre, NY) was performed using an LKB vacugene apparatus as recommended by the supplier (LKB Instruments, Gaithersburg, MD). DNA restriction fragments to be used as probes in Southern blotting experiments were separated by gel

electrophoresis and eluted from gel fragments by the procedure of Vogelstein and Gillespie (21). DNA fragments were labeled by the random priming method of Feinberg and Vogelstein (22). Southern hybridizations were performed as recommended by the nylon membrane supplier (Bio-Rad Laboratories, Rockville Centre, NY).

PCB TRANSFORMATIONS

P. putida F39/D was grown on MSB arginine in the presence of toluene with shaking at 30°C until the cells reached a turbidity of 1.0 at 600 nm. The cells were harvested by centrifugation (8,000 X g for 10 min at 4°C), washed in 50 mM Na/KPO₄ buffer (pH 7.25), and resuspended at a turbidity (600 nm) of 1.0 in 50 mM Na/KPO₄ buffer (pH 7.25) supplemented with arginine. *E. coli* JM109 containing cloned genes of the *P. putida* F1 toluene degradative pathway were grown on MSB glucose with thiamine and ampicillin with shaking at 37°C. When the cells reached a turbidity of 0.5 (at 600 nm) IPTG was added to a final concentration of 1.0 mM and growth continued for 1 hr (one doubling time). Cells were harvested as above except that they were resuspended in 50 mM Na/KPO₄ buffer (pH 7.25) supplemented with glucose at a turbidity of 2.0 (600 nm). Cells (50 ml aliquots) were shaken at 30°C overnight with the appropriate chlorinated biphenyl (1 mg). Cell cultures were then extracted three times with an equal volume of ethyl acetate (150 ml total volume). Each culture was acidified and extracted three more times with equal volumes of ethyl acetate. Extracts were dried over anhydrous sodium sulfate and evaporated to approximately 2.0 ml under vacuum at 30°C. The extracts were then evaporated to dryness under a stream of nitrogen at room temperature in a small glass vial. Each residue was resuspended in 100 µl methanol.

CHEMICAL ANALYSES

Thin layer chromatography was performed with a solvent system of chloroform and acetone (80:20 v/v) using silica gel plastic plates (Eastman Kodak, Rochester, NY). Products were localized under ultraviolet light (254 nm) followed by spraying with Gibb's reagent (2,6-dichloroquinone-4-chloroimide, 3.0% in methanol). Catechols were identified by a strong purple color and phenols by a bright blue color after heating at 80°C for 10 min.

Acetonide derivatives were synthesized to confirm the *cis*-relative stereochemistry of dihydrodiol metabolites (23). Dihydrodiols were dissolved in 2.0 ml dimethoxypropane at 0°C. A crystal of *p*-toluene sulfonic acid was added to initiate the reaction. Anhydrous sodium carbonate (100 mg) was added after 1 hr and stirred for 10 min. Benzene (2 ml) was added and the reaction mixture filtered through a sintered glass funnel to remove solid material. The filtrate was evaporated under a gentle stream of nitrogen and the residue was redissolved in a small quantity of chloroform.

Compounds were analyzed by gas chromatography followed by mass spectroscopy (Hewlett Packard 5890 with MS 5970) equipped with a 25 m Ultra

HP-1 column (0.2 mm x 0.33 μ m film thickness). The injector, oven, and detector temperatures on the gas chromatograph were 175°C, 70°C, and 280°C, respectively. Samples were run with a gradient program starting at 70°C and ending at 280°C at a rate of 10°C per min. The carrier gas was Helium (1 ml/min).

CHEMICAL SOURCES

Biphenyl was obtained from Aldrich Scientific (Milwaukee, WI). 2,3-Dihydroxybiphenyl was a gift from General Electric Co. (Schenectady, NY). 2-Hydroxybiphenyl, 3-hydroxybiphenyl, 2,3-dichlorobiphenyl, 2,4-dichlorobiphenyl, 2,5-dichlorobiphenyl, and 3,4-dichlorobiphenyl were obtained from Ultra Scientific (North Kingstown, RI). 2-Chlorobiphenyl and 3-chlorobiphenyl were obtained from Chemicals Procurement Laboratories, Inc. (College Point, NY) while 4-chlorobiphenyl was obtained from Aldrich Scientific (Milwaukee, WI). cis-2,3-Dihydroxy-1-phenyl-cyclohexa-4,6-diene was prepared using a cis-dihydrodiol-accumulating mutant strain of Beijerinckia (B8/36) according to published procedures (24).

RESULTS

SOUTHERN BLOT ANALYSES

It was previously shown (12) based on nucleotide sequence analysis that the genes for P. putida Fl cis-toluene dihydrodiol dehydrogenase (todD) and 3-methylcatechol 2,3-dioxygenase (todE) were 61% homologous with the genes for P. pseudoalcaligenes KF707 cis-biphenyl dihydrodiol dehydrogenase (bphB) and 2,3-dihydroxybiphenyl 1,2-dioxygenase (bphC). No direct analysis could be made of the homology between the genes for P. putida Fl toluene dioxygenase (todC1C2BA) and the genes for P. pseudoalcaligenes KF707 biphenyl dioxygenase (bphA) since no nucleotide sequence has been published for any biphenyl dioxygenase. We decided therefore to analyze whether the biphenyl degradation genes from another PCB degrading strain, Pseudomonas sp. LB400, were homologous to the toluene degradation genes of P. putida Fl by Southern blot analysis. Plasmid pDTG351 (16,17; Figure 2) contains the todC1C2BADE genes. Based on the nucleotide sequence (12) the region from the EcoRI site to the first BglII site contains the genes for the three components of toluene dioxygenase (todC1C2BA) and the region from the first BglII site to the first XhoI site contains the genes for cis-toluene dihydrodiol dehydrogenase and 3-methylcatechol dioxygenase (todDE). Two radioactive probes were prepared using DNA located between the restriction sites mentioned above. One probe contained the todC1C2BA genes and the other contained the todDE genes. Plasmid pGEM456 (11) cleaved with PstI was the target DNA. This plasmid contains the bphABC genes cloned from Pseudomonas sp. LB400 (11). As can be seen in Figure 3, the probe prepared from the todC1C2BA genes hybridized to three PstI fragments (1.9, 1.6, 0.3 kilobase pairs) from pGEM456 while the probe prepared from the todDE genes hybridized to a single PstI fragment (2.1 kilobase pairs). Thus, the P. putida Fl genes for the conversion of toluene to 3-methylcatechol (todC1C2BADE) are structurally

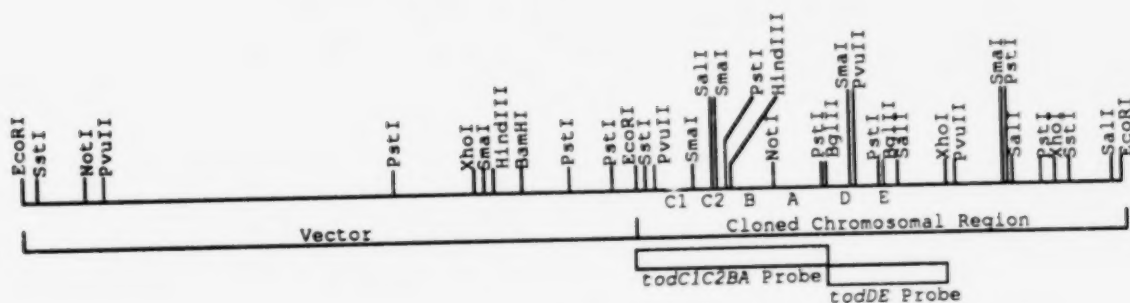
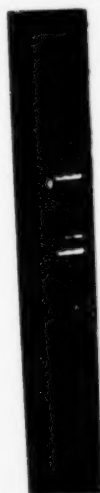


Figure 2. Restriction map of pDTG351. The locations of the todC1C2BADE genes are indicated.

1 2 3 4



Lane 1: 1 kilobase pair DNA standard (Bethesda Research Laboratories Inc., Gaithersburg, MD).

Lane 2: pGEM456 cut with PstI.

Lane 3: pGEM456 cut with PstI and blotted with the todC1C2BA genes.

Lane 4: pGEM456 cut with PstI and blotted with the todDE genes.

Figure 3. Southern blot showing homology between bphABC genes and todC1C2BADE genes.

similar to the Pseudomonas sp. LB400 genes for the conversion of biphenyl to 2,3-dihydroxybiphenyl.

DIHYDRODIOL FORMATION FROM CHLORINATED BIPHENYLS

The Southern blot experiments outlined above demonstrated homology between the aromatic hydrocarbon degradation genes from P. putida F1 and Pseudomonas sp. LB400. However, structural homology does not imply functional homology. Enzymes may show homology with one another but still have different substrate specificities (12). Therefore, the cis-toluene dihydrodiol-accumulating strain P. putida F39/D (derived from strain F1) and E. coli JM109(pDTG601) (containing the todC1C2BA genes) were utilized to determine if the substrate range of toluene dioxygenase extended to

chlorinated biphenyls.

The above strains were first tested for their ability to oxidize biphenyl to cis-biphenyl dihydrodiol. The two strains were grown, induced, and incubated with biphenyl as described in the Materials and Methods section. Product accumulation was monitored by taking an absorption spectrum of culture supernatants at appropriate time intervals. After the transformation, reaction products were extracted and analyzed. No residual biphenyl was detected in the extracts, indicating complete conversion to product. The oxidation product cis-2,3-dihydroxy-1-phenyl-cyclohexa-4,6-diene was identified using thin layer chromatography and gas chromatography followed by mass spectroscopy by comparison to the authentic compound. In addition, 2-hydroxybiphenyl and 3-hydroxybiphenyl were identified by the same techniques as the products formed by acid-catalyzed dehydration of the cis-biphenyl dihydrodiol. The cis-relative stereochemistry was confirmed following the preparation and identification of an isopropylidene derivative (23,24).

Several simple PCBs were chosen for initial analyses of the ability of toluene dioxygenase to oxidize chlorinated biphenyls. The single chlorinated biphenyls: 2-chlorobiphenyl, 3-chlorobiphenyl, and 4-chlorobiphenyl were all readily oxidized to products by toluene dioxygenase utilizing either *P. putida* F39/D or *E. coli* JM109(pDTG601) (Table 1). In addition, the dichlorinated biphenyls: 2,3-dichlorobiphenyl, 2,4-dichlorobiphenyl, 2,5-dichlorobiphenyl, and 3,4-dichlorobiphenyl were also readily oxidized by both organisms. Gas chromatography followed by mass spectroscopy of the products formed showed molecular ions characteristic of dihydrodiols formed from each chlorinated substrate (Table 1). In addition, each dihydrodiol formed an isopropylidene derivative indicating a cis-relative stereochemistry of hydroxyl groups. Analysis of the acid-catalyzed dehydration products formed from the cis-dihydrodiols was conducted by gas chromatography followed by mass spectroscopy. The results showed that two phenols were formed from each dihydrodiol (Table 2). These products are analogous to the 2- and 3-hydroxybiphenyls formed from cis-biphenyl dihydrodiol and confirm the dihydrodiol structures of the initial

TABLE 1. GAS CHROMATOGRAPHY / MASS SPECTROSCOPY ANALYSIS OF CIS-DIHYDRODIOLS FORMED FROM CHLORINATED BIPHENYLS*

Cl-	Rt	m/e (% of base peak)					Isotope Intensity		
							P	P+2	P+4
2-	17.1	222(15)	204(100)	169(76)	141(43)		100%	28%	
3-	18.4	222(11)	204(100)	188(57)	169(50)	141(35)	100%	23%	
4-	18.2	222(11)	204(100)	188(30)	169(41)	141(35)	100%	35%	
2,3-	19.2	256(32)	227(69)	172(34)	165(100)	128(58)	100%	76%	18%
2,4-	18.9	256(39)	227(67)	172(68)	165(100)	128(74)	100%	73%	10%
2,5-	18.9	256(34)	227(73)	172(36)	165(100)	128(73)	100%	74%	14%
3,4-	20.1	256(65)	238(100)	228(51)	184(51)	128(69)	100%	70%	18%

*Abbreviations: Cl, chlorine position on biphenyl; Rt, retention time; m/e, molecular ion; P, parent ion.

TABLE 2. GAS CHROMATOGRAPHY / MASS SPECTROSCOPY ANALYSIS OF
PHENOLS FORMED BY ACID-CATALYZED DEHYDRATION OF
CIS-DIHYDRODIOLS FORMED FROM CHLORINATED BIPHENYLS*

Cl-	Rt	m/e (% of base peak)				Isotope Intensity		
						P	P+2	P+4
2-	15.1	204(62)	169(100)	141(28)	115(19)	100%	32%	
	16.9	204(100)	169(7)	141(15)	115(10)	100%	32%	
3-	16.0	204(94)	169(100)	141(35)	115(24)	100%	28%	
	17.8	204(100)	169(5)	141(17)	115(8)	100%	32%	
4-	16.0	204(100)	169(75)	141(30)	115(20)	100%	32%	
	17.9	204(100)	169(4)	141(17)	115(8)	100%	33%	
2,3-	17.3	238(99)	203(83)	168(100)	139(51)	100%	64%	11%
	18.9	238(100)	203(3)	168(24)	139(22)	100%	79%	12%
2,4-	17.0	238(74)	203(70)	168(100)	139(43)	100%	56%	10%
	18.6	238(100)	202(2)	168(24)	139(22)	100%	70%	12%
2,5-	17.0	238(85)	202(55)	168(100)	139(51)	100%	75%	12%
	18.5	238(100)	202(3)	168(23)	139(20)	100%	65%	11%
3,4-	18.3	238(99)	203(45)	168(100)	139(37)	100%	69%	13%
	19.8	238(100)	202(3)	168(17)	139(12)	100%	76%	12%

*Abbreviations: Cl, chlorine position on biphenyl; Rt, retention time; m/e, molecular ion; P, parent ion.

products. No metabolites were formed when *P. putida* F39/D and *E. coli* JM109(pDTG601) were incubated with chlorinated biphenyls containing more than two chlorine substituents.

CATECHOL FORMATION FROM CHLORINATED BIPHENYLS

In order to further study the substrate range of the enzymes of the toluene dioxygenase pathway we analyzed the ability of *cis*-toluene dihydrodiol dehydrogenase to dehydrogenate the *cis*-dihydrodiols (Table 3). In this case the recombinant *E. coli* strain JM109(pDTG602) was utilized. This strain contains the cloned genes for both toluene dioxygenase (*todC1C2BA*) and *cis*-toluene dihydrodiol dehydrogenase (*todD*). Therefore, any product formed from toluene dioxygenase *in vivo* will be acted upon by the dehydrogenase to form the corresponding catechol. A feasibility study was first conducted with biphenyl. *E. coli* JM109(pDTG602) was grown, induced, and incubated with biphenyl as described above. Transformation products were extracted and analyzed as described in the Materials and Methods. The only product detected by either thin layer chromatography or gas chromatography followed by mass spectroscopy was 2,3-dihydroxybiphenyl. Authentic 2,3-dihydroxybiphenyl had properties identical to those of the bacterial metabolite.

The monochlorinated and dichlorinated biphenyls which were shown to be oxidized by toluene dioxygenase to *cis*-dihydrodiols were also tested with *E. coli* JM109(pDTG602) to determine if catechol compounds could be formed. Each of the chlorinated compounds tested showed a single product with a molecular ion corresponding to a dihydroxylated product of the

TABLE 3. GAS CHROMATOGRAPHY / MASS SPECTROSCOPY ANALYSIS OF
CATECHOLS FORMED FROM CHLORINATED BIPHENYLS*

Cl-	Rt	m/e (% of base peak)				Isotope Intensity		
						P	P+2	P+4
2-	17.3	220(91)	185(100)	157(17)	128(25)	100%	35%	
3-	18.4	220(100)	185(86)	157(17)	128(25)	100%	33%	
4-	18.5	220(100)	185(72)	157(15)	128(21)	100%	37%	
2,3-	19.5	254(95)	219(54)	184(100)		100%	72%	14%
2,4-	19.2	254(76)	219(61)	184(100)		100%	68%	12%
2,5-	19.3	254(65)	219(39)	184(100)		100%	69%	11%
3,4-	20.7	254(88)	219(49)	184(100)		100%	75%	13%

*Abbreviations: Cl, chlorine position on biphenyl; Rt, retention time; m/e, molecular ion; P, parent ion.

starting chlorinated biphenyl (Table 3). Thus, *P. putida* Fl is capable of metabolizing certain chlorinated biphenyls to the corresponding catechols by the enzymes of the toluene dioxygenase pathway.

DISCUSSION

P. putida Fl is capable of growing on a variety of aromatic hydrocarbons as the sole source of carbon and energy for growth. The pathway by which this strain degrades such compounds is shown in Figure 1B. Toluene is first oxidized to *cis*-1(S),2(R)-dihydroxy-3-methylcyclohexa-3,5-diene by the action of toluene dioxygenase. Subsequently this product is dehydrogenated by *cis*-toluene dihydrodiol dehydrogenase to form 3-methylcatechol, the substrate for *meta* ring cleavage by 3-methylcatechol 2,3-dioxygenase. This pathway is chemically analogous to that utilized by *Pseudomonas* sp. LB400 in the metabolism of biphenyl and various PCBs (Figure 1A). In the present work we have shown that the genes for toluene dioxygenase (*todC1C2BA*), *cis*-toluene dihydrodiol dehydrogenase (*todD*), and 3-methylcatechol dioxygenase (*todE*) show homology to the analogous genes from the *Pseudomonas* sp. LB400 PCB degradation pathway (*bphABC*). In addition, toluene dioxygenase was shown to be able to oxidize several chlorinated biphenyls to *cis*-dihydrodiols. Such products could be acted upon by *cis*-toluene dihydrodiol dehydrogenase to form dihydroxy chlorinated biphenyls (catechols). The positions of the hydroxyl groups on *cis*-biphenyl dihydrodiol and dihydroxybiphenyl formed by toluene dioxygenase were determined to be on the second and third carbon of one of the aromatic rings by comparison with known standards. By analogy, oxidation of the chlorinated biphenyls tested with toluene dioxygenase in this study probably occurred at the same positions. We suspect also that such oxidation occurred on the aromatic ring that did not contain any chlorine atoms. We are currently investigating whether this is actually the case. The chlorinated biphenyls oxidized by toluene dioxygenase were limited to those containing one or two chlorine substituents. Toluene dioxygenase does not show the broad PCB substrate specificity of the *Pseudomonas* sp. LB400 enzyme or the analogous enzyme from *Alcaligenes eutrophus* H850 (8,9).

Consequently, Pseudomonas sp. LB400 and A. eutrophus H850 remain the organisms of choice for future studies on the degradation of chlorinated biphenyls that contain several chlorine substituents.

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USE OF DNA HYBRIDIZATION PROBES IN THE MONITORING OF BIOTREATMENT SYSTEMS

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ABSTRACT

As the result of recent technological advances, significant potential now exists for the application of DNA hybridization probes in characterizing complex microbial communities. A review is presented of relevant methodologies now available for such analyses as well as examples of their use. In conjunction with other currently ongoing studies at the U.S. Environmental Protection Agency's Risk Reduction Engineering Laboratory on the treatability of toxic organic compounds, we are initiating studies to apply DNA probe methods towards the characterization of resident microbial communities in wastewater treatment systems. The objectives of this work will include 1) the development of DNA hybridization probes that specifically detect organisms with degradative capabilities toward different toxic chemicals in these communities, 2) the establishment of hybridization probe-based methodologies for determining abundances of these organisms in the communities, 3) the assessment of correlative relationships between the occurrence of these organisms and actual degradative rates by the communities and 4) the identification of adaptive response mechanisms by the communities to high concentrations of toxic chemicals.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Increasingly stringent federal and state regulations concerning the levels of hazardous organic chemicals which may be discharged from municipal and industrial wastewater treatment facilities as well as from a vast number of waste sites are creating new challenges for the design and operation of effective yet economical treatment systems. Advances in bioreactor designs as well as in the identification and development of microorganisms with priority pollutant degradative capabilities have provided important tools that can be used to meet these challenges. Up to now, however, relatively little effort has been directed towards the characterization of microbial communities within most waste treatment systems without which optimization and the potential of bioremediation can not be realized. This paucity of characterization may be ascribed to both the high complexity of such communities in most instances as well as the inadequacy of traditional methods for performing such determinations. The development of new methods for characterizing microbial communities and the application of these methods in predicting and describing responses to potentially toxic compounds would provide a means by which to improve upon the design, operation and development of waste treatment systems.

In recent years, considerable research effort has been directed toward the application of DNA hybridization probes for both the identification and enumeration of specific microorganisms and genotypes in environmental settings. Hybridization probes are functionally single-stranded nucleic acid molecules (usually DNA) that have been labeled in a manner that allows their detection. They are used to identify homologous single-stranded DNA or RNA molecules in heterogeneous mixtures of nucleic acids from various target sources. Much of the impetus for these studies has been the recognized need for monitoring genetically engineered organisms following their release into the environment (1). With an ever-increasing number of isolated genes coding for characteristic properties of different microorganisms becoming available as potential probes, the utilization of this technology for monitoring natural organisms in different environments is also likely to increase. Comparative nucleotide sequencing analysis of ribosomal RNAs or of ribosomal RNA genes is another technology which is rapidly gaining acceptance for use in determinative microbiology (2,3). While to date, phylogenetically-based hybridization probes generated from this growing data base have been used only sporadically in characterizing microbial communities in environmental samples, the potential applications for such probes appear great.

This report will review various methodologies that are now available for the use of DNA hybridization probes in detecting and enumerating specific microorganisms or genes in environmental samples. Examples, where available, will also be presented of applications of these methods in the prediction and analysis of microbial community responses to hazardous chemicals. These studies have thus far shared the feature of employing probes for functional degradative genes. Current limitations of this approach, which will be discussed, have led our laboratory to initiate feasibility studies on the use of phylogenetically-based probes derived from small subunit ribosomal RNA (ssrRNA) in addition to functional gene probes

for performing such evaluations. Potential advantages and disadvantages of this new approach will also be discussed.

METHODOLOGIES

Hybridization probes are usually labeled by the incorporation of radioactive isotopes into their structures, however, a number of nonisotopic labeling procedures have also been developed. Hybridization results from the formation of hydrogen bonds between sequences of homologous base residues present in the probe and corresponding molecules from the target source, i.e., guanine bonds with cytosine and adenine bonds with thymine in DNA, or with uracil in RNA. Practical demonstration of hybridization between probe and target source molecules involves fixing the target nucleic acids to supports, such as nylon membranes prior to incubation with the probe, in which case probe molecules also become fixed to the support upon hybridization. Hybridization is demonstrated and under appropriate conditions quantified by label retention on the support.

The majority of DNA probe applications related to environmental studies have utilized the colony hybridization method. While several modifications of the original procedure of Grunstein and Hogness (4) have been reported, its underlying principles have remained constant. In this procedure, portions of microbial colonies which have been cultivated on agar medium are transferred to the support membranes by a process analogous to replica plating. The cells on the membrane are then lysed *in situ* to release their DNA contents which are concomitantly denatured to a single-stranded form and then bound to the membrane. The membrane is then incubated with the probe DNA and hybridization of probe molecules to homologous target sequences from the individual colonies is detected as described above. Various applications of this procedure have demonstrated both its versatility and sensitivity which, using appropriate conditions, can approach one in 10^8 colonies (5). The primary limitation of this protocol is its requirement for prior cultivation of the microorganisms on a given artificial medium. It is widely recognized that only a small portion of the microorganisms occurring in many natural habitats are amenable to such cultivation (6,7). Additional problems associated with this procedure include variability in the conditions required to obtain satisfactory lysis of different microorganisms and occasionally high noise to signal ratios associated with non-specific binding of the probe to cellular debris from the colonies.

The limitations associated with detection and enumeration procedures requiring prior cultivation of microorganisms from environmental samples have led to the development of methods that allow hybridization of DNA probes with nucleic acids that have been directly isolated from such samples. Methods for the isolation of DNA from soil and sediment samples which have proven to be particularly refractory to such analyses have recently been developed. These methods alternatively employ a preliminary step in which microbial cells are separated from the samples prior to isolation of their DNA (8,9) or direct lysis of the cells and isolation of their DNA from these samples (8,10). Efficiencies of DNA recovery have been shown to be higher using the latter procedure (8), however, DNA isolated by

both methods has been shown to be amenable to qualitative and quantitative analysis for the presence of specific organisms or genotypes (9,10). The hybridization analyses are characteristically performed in a similar fashion to colony hybridization analyses wherein the DNA isolated from the soil or sediment samples is denatured and bound to a membrane support prior to incubation with the probe. Quantitation is achieved by comparing the amounts of label retained by known amounts of total sample DNA to a standard curve. The curve is generated from different amounts of the specific target DNA incubated simultaneously with the probe. Detection limits for target sequences using this approach have ranged in different studies from 0.2 pg to 2 ng/ug total DNA (9,11). These variations are likely to be in large part attributable to differences in probe labeling efficiencies resulting from the use of different labeling methods (9). Experiments involving the additions of known numbers of organisms containing target DNA sequences to soil and sediment samples have also been used to estimate the sensitivity of these analyses (9,12). While differences in the ratios of target to non-target organisms have the potential to significantly affect such estimates, the values reported in these studies have coincided fairly closely at approximately 10^4 cells/gram of sample.

This degree of sensitivity, while useful for many applications, may be insufficient for the detection of many microbial strains or genotypes present in low numbers or in a high background of non-target organisms. Recent studies have demonstrated, however, that target DNA sequences can be specifically amplified within heterogeneous DNA mixtures by employing the polymerase chain reaction or PCR procedure (12). Target DNA amplification by this procedure has been shown to increase the sensitivity of DNA probe hybridization analyses for detecting specific organisms by at least 100-fold.

FUNCTIONAL GENE PROBES

Hybridization analyses using DNA probes can provide descriptive information concerning the composition and functional attributes of microbial communities with a minimum of time and effort. Consequently, these analyses would find numerous uses in monitoring alterations and adaptive responses of microbial communities resulting from their exposure to toxic chemicals. Perhaps of greater practical importance, however, is the potential predictive information available from these analyses for determining the degradative capabilities of different microbial communities toward such chemicals. While it is known that numerous factors can affect degradative activity, considerable effort has been directed towards examining the correlation between the occurrence of appropriate genotypes and actual degradation. Studies on the relative numbers of colony-forming organisms that hybridized with a probe consisting of the entire naphthalene degradative plasmid, Nah 7, showed a 30-fold higher level of such organisms in a sediment sample that had previously been exposed to a mixture of hydrocarbons compared with in an unexposed sediment sample from the same source (13). These results corresponded with a 15-fold higher rate of naphthalene mineralization by the microbial community in the exposed sample. Similarly, changes in the abundance of colony-forming organisms that hybridized with the Nah 7 plasmid probe were found to closely approximate

changes in naphthalene mineralization in a continuously-operated bioreactor (11). Other studies have been performed using DNA probes for Hg^{2+} -resistance(*mer*) genes. Genes of this type are involved in the reduction of Hg^{2+} to elemental mercury (Hg^0) which results in rapid elimination of this chemical by volatilization. Hybridization analyses using *mer* gene probes showed significantly higher frequencies of these genes in DNA samples directly extracted from Hg^{2+} -contaminated freshwater and sediment samples than in similar DNA extracts from corresponding uncontaminated samples (14,15). These results were shown to correlate with higher rates of Hg^0 volatilization and higher frequencies of Hg^{2+} -resistant organisms occurring in the contaminated samples.

Such studies have thus far indicated that hybridization analyses using functional gene probes may in some but not all instances provide predictive information concerning the ability of microbial populations to degrade or otherwise eliminate toxic chemicals. While as stated earlier, numerous factors in addition to the frequencies of such genes can affect overall rates of these processes, current evidence suggests that in most instances where the results of hybridization analyses have proven to be non-predictive, other isofunctional but non-homologous genes may have been present in the microbial communities. This point can be illustrated in studies on Hg^{2+} -resistant organisms from several saltwater communities (15,16). In each instance the frequencies of Hg^{2+} -resistant organisms as determined by platings on Hg^{2+} -containing media were shown to correlate with Hg^0 volatilization rates by these communities. Hybridization analyses showed, however, that the large majority of these resistant organisms did not contain genes which were homologous to the available *mer* gene probes. Similarly, studies on toluene degradation in a groundwater aquifer microcosm showed that this activity could not be correlated with the frequency of organisms that hybridized to a toluene degradative gene probe originating from the Tol plasmid (17). Other studies have shown, however, that at least three distinct pathways for toluene degradation in addition to the pathway encoded for by the Tol plasmid exist in different bacteria (18-21). Since it is unlikely that the genes specifying these pathways would show homology to Tol plasmid genes, such organisms would not have been identified in these studies. These examples show that the use of functional gene hybridization analyses for accurate predictive assessments of a microbial community's degradative capability requires probes for all of the relevant genotypes that may be present in the community. In many instances, this technology may therefore not yet be applicable due to the unavailability of the appropriate probes.

PHYLOGENETICALLY-BASED PROBES

Comparative nucleotide sequence analysis of *ssr*RNAs has become recognized as a highly useful method for defining phylogenetic relationships between different organisms. Such relationships have been inferred from observations that different portions of these universally-occurring molecules undergo nucleotide sequence divergence at different evolutionary rates (3). An important offshoot of this research has been the recognition that this variability of nucleotide sequence conservation in different portions of *ssr*RNA molecules can form the basis for the construction of DNA

hybridization probes, specific for various phylogenetic groupings from the kingdom down to the subspecies level (22-26). In addition, these analyses have provided the basis for the development of new methods that allow the rapid determination of *ssrRNA* sequences (26,27).

Due to the recent nature of these developments, the data base of sequenced *ssrRNAs* for different organisms is still relatively small and the number of studies using hybridization probes generated from this data base to evaluate microbial communities in natural environments is even smaller. The applicability of such an approach, however, has been recently illustrated in an analysis of the responses of various strains of *Bacteroides succinogenes* and *Lachnospira multiparus*-like organisms in a bovine rumen that were exposed to the ionophore antibiotic, monensin, using several species and group-specific probes (23). As in hybridization analyses using directly extracted DNA, the detection and enumeration of *ssrRNA* sequences does not require prior cultivation of organisms from the communities under investigation. In addition, methods have been recently described which would allow for the sequencing and construction of probes for *ssrRNAs* from non-culturable organisms (26,28).

TOWARDS THE DEVELOPMENT OF A COMPREHENSIVE MONITORING SYSTEM BASED ON DNA HYBRIDIZATION PROBES

As previously discussed, determinations of functional degradative gene frequencies show promise as predictive indicators of the degradative capabilities of microbial communities toward hazardous chemicals, provided that gene probes for all of the relevant degradative pathways are available. In instances where such probes are not available, *ssrRNA*-specific probes for phylogenetic groups with demonstrated degradative capabilities towards the compounds in question may be a practical alternative. In view of the rapid procedures now available for obtaining *ssrRNA* sequence information from both culturable and non-culturable organisms, and, because this technology does not require extensive preliminary characterization of the genes involved, the amounts of time and effort required for the development of such probes should be relatively small. Significant questions remain, however, concerning the usefulness of such probes, particularly in the field of biodegradation research. These stem in part from current uncertainties as to the specificity of such probes, particularly at the sub-species level. It can be anticipated that *ssrRNA* sequence information for large numbers of new microbial species and strains will be added to the presently existing data base in the near future which should clarify much of this uncertainty. Of potentially greater importance is the question of whether specific degradative capabilities are universally associated with specific phylogenetic groups. For example, it has been well documented that degradative genes for a number of toxic and/or synthetic compounds are carried on transmissible plasmids which do not necessarily occur within all members of a given phylogenetic group (29). Conversely, there is presently a great need to further establish the role of degradative gene transmission (via plasmids or other means) within microbial populations as a possible adaptive mechanism in community responses to toxic chemicals.

Our laboratory has been involved in the isolation, from different

activated sludge sources, of microbial strains that show degradative activity toward several pollutant chemicals. As shown in Table 1, the majority of these test compounds are degraded by a number of distinct microbial strains which in all likelihood do not yet represent all of the

TABLE 1. NUMBERS OF INDEPENDENT BACTERIAL STRAINS SHOWING CATABOLIC ACTIVITIES TOWARD AROMATIC HYDROCARBON TEST COMPOUNDS FROM TWO WASTEWATER TREATMENT SYSTEMS^{1,2}

Test Compound	Source of strains	
	BP ³	HL ⁴
Toluene	7	3
Benzene	5	5
Ethyl Benzene	5	2
Phenol	8	12
o-Cresol	3	ND
2,4-Dimethylphenol	2	0
Dimethylphthalate	0	2
Diethylphthalate	0	2
Dibutylphthalate	0	2
Phthalic acid	6	ND

¹ Catabolic activity established on the basis of growth in the presence of the test compounds as sole carbon sources.

² Strains differentiated by comparisons of agarose gel electrophoretic banding patterns of total genomic DNA fragments following digestion with restriction endonucleases.

³ Activated sludge from a wastewater treatment system at the British Petroleum facility in Lima, Ohio.

⁴ Activated sludge from a wastewater treatment facility at the Hoffman-LaRoche facility in Nutley, New Jersey.

ND: not determined

organisms from these communities with such capabilities. Our initial goal will be to establish phylogenetic relationships between these and other degradative strains as they are isolated based on both traditional determinative methods such as the API and Biolog test systems as well as by comparative analyses of their ssrRNA nucleotide sequences.

The sequence data will subsequently be used to construct DNA oligonucleotide probes that are specific to each of the phylogenetic groups identified. These probes will then be used to determine the distributions in the original sludge populations of specific degradative phenotypes within each phylogenetic group. They will also be used to determine the frequency of organisms specific to each group within the total sludge microbial communities and whether these frequencies show correlations with the degradative activity exhibited by these sludge communities toward the different test compounds. Where available, DNA hybridization probes for relevant functional degradative genes will also be employed in parallel analyses.

In addition to these studies, samples of the original sludges will be used to inoculate continuously-operated bench scale bioreactors fed with sterilized conventional wastewater and varying loads of the test compounds. Monitoring of the microbial populations within these reactors will again be performed by hybridization analyses using phylogenetic and functional gene-specific probes. These studies will be used to further assess the extent of correlation between degradative activity and the frequencies of these organisms and/or genes within the overall microbial communities as well as to identify adaptive response mechanisms within these communities to high concentrations of the different compounds.

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BIODEGRADABILITY STUDIES OF THE ALASKAN WEATHERED CRUDE OIL CONSTITUENTS
WITH THE USE OF ELECTROLYTIC RESPIROMETRY AND SHAKER FLASK SYSTEMS

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ABSTRACT

Bench-scale biodegradability studies of the Alaskan weathered crude oil constituents were undertaken as part of the overall bioremediation project for the shorelines of Prince William Sound, Alaska, contaminated by the Exxon oil spill. The purpose of the studies was to evaluate the capability of the indigenous microbial consortium of the sea water and the coastline and island beach areas in the vicinity of the oil spill, to biodegrade and/or biotransform the spilled weathered crude oil alkane hydrocarbon and polynuclear aromatic (PAH) constituents in batch-type respirometric reactors and shaker flask systems.

The specific objectives of the current studies were to utilize the electrolytic respirometry oxygen uptake and shaker flask gas chromatographic analytical data in order to: (1) determine the biodegradability of the alkane and PAH constituents of the weathered crude oil by the indigenous microbiota, (2) evaluate the capability of varied fertilizer formulations (i.e., oleophilic fertilizer - Inipol, slow release water soluble fertilizer - Sierra, etc.) to serve as nutrients for promoting an effective biotreatment of these organics, and (3) assess any potential inhibitory effects of the crude oil constituents on both the indigenous biomass and their biodegradative activity on readily biodegradable or biogenic substrates. Additionally, studies incorporated the use of Valdez, Alaska waste treatment plant oil bilge biomass to determine its capacity to bio-oxidize the weathered crude oil constituents.

The data obtained which demonstrate almost complete utilization of the alkane hydrocarbon constituents in presence of Inipol EAP 22 fertilizer and very significant biodegradation of the PAH constituents in the culture media after 6 weeks of incubation. Growth data indicate significant increase of growth of indigenous oil degrading microbiota (increase of 4 to 6 orders of magnitude) at the end of 6-week incubation period. Results from shaker flasks

based on growth data and on the GC scans and GC/MS analysis data for the alkane hydrocarbons and PAH constituents of the weathered crude oil demonstrate similar significant biodegradation of PAHs and complete dissimilation of alkane hydrocarbons in presence of Inipol in culture media after 6 weeks of incubation.

Control respirometric and shaker flask experiments without Inipol EAP 22 provided data that demonstrate absence of biodegradative activity of the microbiota on the alkane hydrocarbons and PAHs oil components.

INTRODUCTION

The U.S. EPA Alaska Bioremediation Project was initiated in the aftermath of the March 24, 1989, Exxon Valdez oil spill in Prince William Sound, Alaska. Hydrocarbon-degrading bacteria are known to exist in the waters and sediments of the Prince William Sound, but in the presence of large amounts of degradable petroleum, the growth and activity of the bacteria becomes limited by the availability of nitrogen and phosphorus. The objective of the bioremediation project was to determine if techniques for accelerating the hydrocarbon bioremediation rates through the use of indigenous, mixed populations of hydrocarbon-degrading microorganisms can be utilized in the cleanup of the spill and to demonstrate a method of enhancing the cleanup of oil contaminated shorelines by adding nutrients to stimulate the growth of naturally occurring oil-degrading microbiota.

The bioremediation project was composed of four complementary field studies: (1) a beach substrate study which attempted to assess the quantity and constituents of the oil in the substrate and their change over time (by determination of decrease of C17:pristane ratio, and the C18:phytane ratio in case of alkane hydrocarbons and the biodegradability rates of polycyclic aromatic hydrocarbons); (2) a nutrient addition project to evaluate the success of applying different nutrient additions (inorganic nitrogen and phosphorus) that are expected to enhance the biodegradation of the contaminant oil; (3) a microbiology study to assess the effect of the fertilizers on the stimulation of oil-degrading bacteria both in the oil-bearing substrate and in the interstitial water within the substrate, and to significantly increase the population of oil degrading microbiota; and (4) a longer term assessment to evaluate the effects of the treatment on the Prince William Sound beaches and waters.

Laboratory bench-scale biodegradability studies of the Alaskan weathered crude oil constituents using closed systems were undertaken as part of the overall bioremediation project.

The specific objectives of the current studies were to utilize the electrolytic respirometry oxygen uptake and shaker flask gas chromatographic analytical data in order to: (1) determine the biodegradability of the alkane and PAH constituents of the weathered crude oil by the indigenous microbiota, (2) evaluate the capability of varied fertilizer formulations to serve as nutrients for promoting an effective biotreatment of these organics, and (3)

assess any potential inhibitory effects of the crude oil constituents on both the indigenous biomass and their biodegradative activity on readily biodegradable or biogenic substrates. Additionally, samples of the Alyeska Ballast Water Treatment Plant sludge were evaluated as enhancements to the natural microbiota for biodegrading the oil.

Analytical respirometry served as the primary experimental approach for studying the rates of biodegradation of oil constituents. Supplementing the analytical respirometry experiments were batch flask microcosms to provide additional testing of the biodegradability of the individual aliphatic and aromatic constituents of the crude oil.

In addition to the oxygen uptake (consumption) measurements generated from the respirometric reactors, GC/MS chromatogram scans of alkane hydrocarbons and GC/MS analysis of aromatic hydrocarbons (PAHs) in aqueous culture sample extracts were taken at various time intervals from respirometric vessels and shaker flask microcosms. This was done to determine which of the oil constituents were biodegraded in the closed reactor systems.

The oleophilic fertilizer, Inipol EAP 22, containing urea as the nitrogen source and lauryl phosphate as the phosphorus source in an oleic acid external phase, and manufactured by Elf Aquitaine, was used as the nutrient fertilizer. The ability of Inipol to provide an adequate amount of nitrogen and phosphorus for the microbial degradation of weathered crude oil was compared to that of the OECD minimal salts medium containing inorganic and water soluble nutrients.

These laboratory experiments were conducted to support the field work, which was much less controllable and much more susceptible to nutrient washout, re-oiling, tidal cycles and washout, temperature variation, climatic changes, freshwater/saltwater interactions, etc., all of which would confound interpretation of the findings.

BACKGROUND

BIODEGRADATION OF PETROLEUM HYDROCARBONS IN MARINE ECOSYSTEMS

The expansion of petroleum development into new frontiers, such as deep offshore waters and ice-dominated arctic environments, and the apparently inevitable spillage which occur during routine operations and as a consequence of acute accidents have dramatically focused an interest on the problems of oil pollution of marine ecosystems.

Most previous reviews concerning the microbial degradation of petroleum pollutants have been concerned with the marine environment (Atlas, 1977; Atlas and Bartha, 1973a; Atlas and Schofield, 1975; Bartha and Atlas, 1977; Colwell and Walker, 1977; Crow *et al.*, 1974; Floodgate, 1972a, 1972b, 1973, 1976; Jordan and Payne, 1980; Karrick, 1977; National Academy of Sciences, 1975; Van der Linden, 1978; ZoBell, 1946, 1964, 1969, 1973). Atlas's review (1982)

expanded the scope to include consideration of the fate of petroleum hydrocarbons in freshwater and soil ecosystems.

ENHANCEMENT OF NATURAL BIODEGRADATION OF CRUDE OIL IN MARINE ENVIRONMENT

The fate of petroleum hydrocarbons in the environment is largely determined by abiotic factors which influence the weathering, including biodegradation of the oil. Factors which influence rates of microbial growth and enzymatic activities affect the rates of petroleum hydrocarbon biodegradation. The persistence of petroleum pollutants depends on the quantity and quality of the hydrocarbon mixture and on the properties of the affected ecosystem. In one environment, petroleum hydrocarbons can persist indefinitely, whereas under another set of conditions, the same hydrocarbons can be completely biodegraded within a relatively few hours or days.

Dispersants

Dispersants have been used to treat oil spills. In some cases the use of toxic dispersants probably has resulted in greater ecological impact than the oil spill itself; such was the case in the Torrey Canyon incident (Cowell, 1971; Smith, 1968). Some dispersants may contain chemicals which are inhibitory to microorganisms. Without toxicity, however, dispersion can enhance petroleum biodegradation. Mulkins-Phillips and Stewart (1974a) found that some dispersants enhanced *n*-alkane degradation in crude oil, but that other dispersants had no effect. Gatellier et al., (1971, 1973) and Robichaux and Myrick (1972) likewise found that some dispersants inhibited hydrocarbon-oxidizing populations, whereas others enhanced hydrocarbon-degrading microorganisms. Atlas and Bartha (1973b) tested several dispersants and found that all increased the rate but not the extent of hydrocarbon mineralization.

Nutrients

There is some confusion and considerable apparent conflict in the literature regarding the limitation of petroleum biodegradation by available concentrations of nitrogen and phosphorus in seawater. Several investigators (Atlas and Bartha, 1972a; Bartha and Atlas, 1973; Floodgate, 1973, 1979; Gunkel, 1967; LePetit and Barthelemy, 1968; LePetit and N'Guyen, 1976) have reported that concentrations of available nitrogen and phosphorus in seawater are severely limiting to microbial hydrocarbon degradation. Other investigators (Kinney et al., 1969), however, have reached the opposite conclusion, i.e., that nitrogen and phosphorus are not limiting in seawater. The difference in results appears to be based on whether the studies are aimed at assessing the biodegradation of hydrocarbons within an oil slick or the biodegradation of soluble hydrocarbons.

Extensive studies have been made which demonstrate enhanced biodegradation of crude oil due to addition of nitrogen and phosphorus [Floodgate (1973), Bridie and Bos (1971), Atlas and Bartha (1972) Reisfeld et al., (1972), Colwell et al., (1978), Ward and Brock (1976), LePetit and N'Guyen (1976), Gibbs (1975), Van Der Linden (1978)]. Oil-degrading microorganisms are ubiquitous and can metabolize a wide range of oil components under diverse

environmental conditions (Atlas, 1981; Mulkins-Phillips and Stewart, 1974b), although the rates of oil biodegradation in the marine environment are generally slow because of the lack of optimal ratios of carbon, nitrogen and phosphorus.

Inoculation "seeding" experiments have repetitively demonstrated that specific cultures of oil-degrading bacteria fail to enhance the hydrocarbon degradation capability of natural environments because they typically disappear from dominant microflora. The indigenous microflora, on the other hand, show a capacity for the adaptation to petroleum degradation within days [Bartha and Atlas (1977); Lee and Levy (1987); Taggar et al., (1983)] under conditions where the rates of petroleum biodegradation is limited by nutrient deficiencies. The beneficial effect of fertilization with nitrogen and phosphorus has been conclusively demonstrated and offers great promise as a countermeasure for combating oil spills [Atlas (1981); Delaune et al (1980); Gibbs and Davis (1970); Olivieri et al. (1976)]. The optimum ratios of carbon, nitrogen and phosphorus to support maximum oil biodegradation ratios have been defined by laboratory studies [Atlas and Bartha (1972); Bridie and Bos (1971)].

The addition of nitrogen- and phosphorus-containing fertilizers can be used to stimulate microbial hydrocarbon degradation. In addition, oleophilic nutrients have been developed to overcome the problem of the water soluble nutrients being rapidly removed from the oil-water interface where biodegradation occurs [Atlas and Bartha (1973c); Sirvins and Angles (1986)].

Bergstein and Vestal (1978) studied the biodegradation of crude oil in Arctic tundra ponds. They concluded that oleophilic fertilizer may provide a useful tool to enhance the biodegradation of crude oil spilled on such oligotrophic waters. Without addition of nitrogen and phosphorus, hydrocarbon biodegradation was limited. Atlas and Bartha (1973c) described an oleophilic nitrogen and phosphorus fertilizer which could overcome limitations of nitrogen and phosphorus in seawater and stimulate petroleum biodegradation in seawater.

Olivieri et al., (1976) described a slow-release fertilizer containing paraffin-supported magnesium ammonium phosphate as the active ingredient for stimulating petroleum biodegradation. They reported that the biodegradation of Sarir crude oil in seawater was considerably enhanced by addition of the paraffin-supported fertilizer. Kator et al. (1972) suggested the use of paraffinized ammonium and phosphate salts for enhancing oil biodegradation in seawater.

Studies of Tramier and Sirvins (1983) generated a unique approach to render the enhancement of oil biodegradation process in marine environment operational. A nutrient including nitrogen, phosphorus and carbon has been developed and formulated as an oleophilic microemulsion. The nutrient has been tested in laboratory and field situations in temperate and cold climates. Biodegradation rates have ranged from 60 percent to 85 percent depending on conditions.

Bronchart *et al.* (1985) developed an oil dispersant with oleophilic nutrients made up of an oleophilic part (normal paraffine and olefine) and of a hydrophilic moiety (containing nitrogen and/or phosphorus) which exhibited a high dispersion efficiency and a quick-starting biodegradation of the dispersed crude oil.

In a study of biodegradation of a weathered crude oil emulsion (Halmö, 1985) direct addition of fertilizer to oil on shore enhanced the natural biodegradation. An oil-soluble urea fertilizer was at least as efficient as a water-soluble one containing ammonia and nitrate. In one year, the paraffins were totally degraded. Composting was studied both in aerated full-scale windrows and in model columns.

Laboratory tests conducted by Lee and Levy (1987) at 3°C and 20°C indicate that biodegradation of a light crude oil (condensate) by indigenous microflora of sandy beach environments can be enhanced by the addition of an oleophilic nutrient. Their field trials conducted over a 204-day period in the intertidal zone of a sandy beach in Atlantic Canada suggest that the most promising approach to enhancing the biodegradation of oil-stained sandy beach environments is through periodic replenishment of nutrients after the indigenous microflora have adapted to the contaminated sediments.

Studies of Sveum (1988) and Sveum and LaDousse (1984) demonstrated that oil exploration in arctic regions will require special oil spill cleanup methods for shorelines. The application of fertilizers to speed biodegradation of oil may hold promise. Inipol EAP 22, an oil-soluble fertilizer that is nontoxic and biodegradable, was tested in a series of experiments on Spitsbergen, Norway, to determine its effectiveness under various conditions. Uptake and exchange of nutrients depends on the complex growth kinetics of the bacteria involved and requires detailed study.

Field experiments (Lee and Levy, 1989), in an aerobic intertidal sandy beach environment (low energy coastal systems), demonstrated that the biodegradation of Scotian Shelf condensate and Hibernia crude oil can be substantially accelerated by periodic application of agricultural fertilizers.

MATERIALS AND METHODS

GENERAL EXPERIMENTAL APPROACH

Nutrient Media

Two nutrient formulations were compared for their ability to support the growth of hydrocarbon degraders on weathered Prudhoe Bay crude oil. The oleophilic fertilizer Inipol EAP 22 contains urea as the nitrogen source and lauryl phosphate as the phosphorus source encapsulated in an oleic acid external phase. Because of its oleophilic nature, it enables the microorganisms to perform their hydrocarbon metabolic activities at an optimum rate at the oil-water surface, and it acts by stimulating the growth of hydrocarbon specific bacteria.

The second nutrient solution used in these studies was an OECD synthetic medium (OECD Guidelines for Testing of Chemicals, OECD, Paris, France, 1981) consisting of measured amounts per liter of deionized distilled water of (1) mineral salts solution; (2) trace salts solution, and (3) a solution (150 mg/L) of yeast extract as a substitute for vitaminsolution.

Microbial Inoculum

The microbial inoculum consisted of seawater from Snug Harbor, beach material collected from an uncontaminated beach in Valdez, and weathered crude oil from the spill. Some vessels and flasks were additionally supplemented with indigenous biomass from the Alyeska ballast water treatment plant.

For seawater source inocula, seawater was used as diluent after appropriate volumes of the stock solutions of the mineral salts medium and yeast extract was added to reactors in addition to the oil (mousse) sample. The sludge biomass from the oil bilge waste treatment system was added to the medium at a concentration of 10 mL or at other desirable concentration levels. Beach sand/rock was added in a measured amount to the bottom of the respirometric vessels and shaker flasks to serve as source of the beach surface and subsurface microbial population. Regardless of the microbial inoculum source, seawater served as the diluent liquid after all nutrients beach sand and the crude oil substrate were added to the respirometric reactors and shaker flask microcosms.

Test and Control Substrates

The test substrate used in the study was the Prudhoe Bay weathered crude oil from the oil polluted beaches of Prince William Sound, containing the alkane, paraffinic, polycyclic aromatic and asphaltic organic constituents. Aniline was used as the biodegradable control reference compound at a concentration level of 100 mg/L in the toxicity control systems.

ANALYTICAL RESPIROMETRY

The electrolytic respirometry approach to determine the biodegradability of the organic test compounds in this study was chosen because of the specific advantages of the respirometric methods over that of manometric procedures in tracking oxygen utilization during the exertion of biochemical oxygen demand (BOD).

A comprehensive description of the procedural steps of the respirometric tests and of the experimental design employing test and control systems is presented elsewhere [OECD Guidelines for Testing of Chemicals (1983), Tabak et al. (1984)].

For fully automatic data acquisition, frequent recording and storage of large numbers of oxygen uptake data, the Sapromat B-12 recorders are interfaced to an IBM-AT computer via the Metrabyte interface system. The use of Laboratory Handbook software package allows the collection of data at 15 minute intervals.

Experimental Design

The typical experimental system consisted of duplicate flasks for three concentrations of weathered crude oil (1,000 mg/L, 300 mg/L and 100 mg/L) each containing Inipol EAP 22 at 5 percent of the oil weight or OECD nutrient concentrate solution (2x standard concentration). All the vessels contained 2 g of uncontaminated beach sand from Valdez, Alaska, and 1,000 mg/L of seawater collected off-shore at Snug Harbor, an inlet on Knight Island in Prince William Sound. In addition, the experimental system incorporated duplicate flasks containing each 1,000 mg/L oil, 10 mL of Alyeska ballast sludge, 2 grams of unpolluted beach sand and Inipol EAP 22 at 5 percent of oil weight, diluted with 1,000 mL of seawater. The respirometric control system consisted of single flasks representing (1) inoculum control; (2) inoculum/nutrient control; (3) toxicity control for testing of toxicity of oil to aniline biodegradation; (4) positive reference control (aniline + oil + seawater + beach sand; (5) abiotic substrate control; (6) no nutrient control; no Inipol); and (7) substrate/nutrient control. The vessels containing beach material, oil and Inipol were charged by first adding the beach sand, then adding the measured amount of oil onto the sand, followed by adding one measured amount of Inipol to the oiled rocks, and finally by filling the vessel with Snug Harbor seawater. The experimental design of the respirometry experiments is summarized in Table 1.

The contents of the reaction vessels were first stirred for an hour to ensure an endogenous respiration state at the initiation of oxygen uptake measurements. The incubation period of the experimental run was extended to 30 weeks.

Incubation Temperature.

The reaction vessels were incubated at 15°C in the dark (enclosed in the temperature controlled waterbath) and stirred continuously throughout the run by magnetic stirrers. This temperature was chosen since it was estimated to be the average summer temperature in Valdez, Alaska.

Respirometric Vessels.

The reaction vessels used in the study were 1,200 mL capacity flasks with two side arms at lower and upper positions to allow intermittent sampling of the aqueous and gaseous phase for residual parent oil component compounds, intermediate and end products of oil metabolism and the liquid phase to determine the growth rate of indigenous microbiota. The total volume of the culture/medium/nutrients/substrate in the respirometric reactor was 1,000 mL. The small amounts of liquid sampled throughout the experimental run did not have any significant effect on the cumulative oxygen uptake values and the generated oxygen uptake velocity curves.

FLASK EXPERIMENTS

Flask microcosms were set-up to provide further support of the respirometric studies. Concentrations of weathered crude oil as high as

10,000 mg/L were used to determine if such levels were inhibitory to the biodegradation process. Thirty 2-liter capacity flasks were integrated into the program consisting of 18 experimental and 12 control flask microcosm systems.

Experimental Design

The experimental system consisted of (1) duplicate flasks for three concentrations of weathered crude oil (10,000 mg/L, 3,000 mg/L and 1,000 mg/L) each containing Inipol EAP 22 at 5 percent concentration of the oil weight (2) duplicate flasks containing 10,000 mg/L weathered crude oil, Inipol EAP22 at 5 percent concentration of oil weight and Alyeska ballast sludge (10 mL) as an additional inoculum supplement; and (3) duplicate flasks containing 10,000 mg/L weathered oil, OECD medium concentrate (2x standard concentration) in place of Inipol EAP 22 as a nutrient and with or without Alyeska ballast sludge (10 mL) as an additional inoculum supplement. Each flask equally contained 20 grams of uncontaminated beach sand from Valdez and 1,000 mL Snug Harbor seawater. The flasks were charged with various additives in the same fashion and order as above. In addition, the experimental system incorporated duplicate flasks for three weights of polluted beach sand (5, 10 and 15 g), each set of duplicates containing Inipol EAP 22 at 2.5, 5.0 and 7.5 mg/L and 1,000 mL of Snug Harbor seawater. The shaker flask control system consisted of single flasks representing inoculum controls; inoculum/nutrient controls; toxicity controls and positive reference controls. The experimental design of the shaker flask experiments are summarized in Table 2.

The flask microcosms were placed on a rotary New Brunswick Shaker and incubated in a dark constant temperature room at 15°C.

ANALYTICAL METHODOLOGY FOR ALKANE HYDROCARBONS AND POLYNUCLEAR AROMATIC HYDROCARBONS

Oil biodegradation in the respirometric reactors was monitored by oxygen consumption data, microbial growth determination, gas chromatography scans and GC/MS analysis whereas the biodegradative activity of the indigenous biomass in the shaker flask was followed by GC/MS analysis, GC scans and by microbial growth determination. Gas chromatographic scans and GC/MS analysis of culture samples from respirometric and shaker flask systems were made at the start of experiments, and after 6 and 30 weeks of incubation. Growth data were based on plate colony counts (cell numbers on marine and weathered crude oil agar plates).

Oil characterization methodology measured individual oil components in the aliphatic and aromatic fractions of oil extracts. The aliphatic fractions were measured by gas chromatography using a flame ionization detector. The aromatic fractions were characterized by gas chromatography/mass spectrometry.

A procedure for sample extraction and fractionation and a methodology for analysis of aliphatic and aromatic hydrocarbons, which was used in these studies, was developed by Nisamaneepong (1989). The analytical protocol is a

modification of the most current procedures used in the analysis of the above hydrocarbons in oil. An established and an EPA acceptable QA/QC protocol for aliphatic and aromatic hydrocarbons was used in the study.

RESULTS

Data included in this paper represent results obtained by analysis of culture samples from respirometric vessels and from shaker flask microcosms as well as results based on oxygen consumption data for the 6- and 30-week incubation period. Biodegradation data reported are those generated from studies that incorporated the use of Inipol EAP 22 as fertilizer nutrient source as well as that of the OECD synthetic medium.

Naturally weathered Prudhoe Bay crude oil collected from the oil contaminated beaches in the Prince William Sound, Alaska, as well as an artificially weathered crude oil from Prudhoe Bay were subjected to GC/FID analysis for alkane hydrocarbons and GC/MS analysis of the aromatic hydrocarbons (PAHs) before the initiation of the respirometric and shaker flask biodegradation studies. Tables 3 and 4 provide a summary of the concentration levels in $\mu\text{g/g}$ (ppm) of the C-8 through C-38 aliphatic hydrocarbon (including pristane and phytane) constituents and polycyclic aromatic hydrocarbon constituents of the naturally and artificially weathered crude oil samples.

ANALYTICAL RESPIROMETRY

Respirometric studies have provided data based on cumulative oxygen uptake data, growth data and GC scans and GC/MS analysis data which demonstrate almost complete biodegradation of the aliphatic hydrocarbons in the presence of the Inipol EAP 22 fertilizer nutrient, and very significant utilization of the PAH hydrocarbons in the culture media after six weeks of incubation.

Oxygen Consumption Data

Respirometric results of the respirometry experiments based on the oxygen uptake data from vessels containing 1,000 mg/L oil and Inipol EAP 22 (5 percent by weight of oil) and from the control respirometric vessel containing only Inipol nutrient as a source of carbon for 66-day incubation periods are summarized in Figure 1. The figure displays cumulative oxygen consumption as a function of time illustrated by oxygen uptake velocity curves for the two reactor systems. Oxygen uptake began on both vessels after only 1.5-days lag period. Maximum oxygen uptake on Inipol alone occurred by the 9th day, leveling off at approximately 150 mg/L. Oxygen uptake rate on the reactor containing weathered oil and Inipol was multiphasic: The first 10 days exhibited the highest uptake rate followed by a slower rate for the next 16 days and a somewhat faster rate for the next 4 days. Maximum cumulative oxygen uptake appears to have occurred by the 30th day, showing a typical plateau of oxygen consumption beyond the 30 days of incubation. Data collection continued well beyond the 66 days shown in the figure and results will be reported subsequently. Figure 2 provides oxygen uptake as a function of time in the inoculum control vessel (beach material + seawater, no oil or

Inipol) and in the substrate control vessel (oil, no Inipol, sterilized beach material and seawater). In the inoculum control system, the endogenous oxygen uptake curve plateaus at a maximum of 18 mg/L, whereas maximum oxygen uptake in the substrate control system is 5-6 mg/L for the 66 days of incubation. Oxygen uptake curves for the no nutrient control vessel (beach material + seawater + oil, no Inipol) and for the substrate/nutrient control vessel (oil, Inipol, sterilized beach material and seawater) are shown in Figure 3. The maximum oxygen uptake values for the two control systems were 24 mg/L and 5-6 mg/L respectively at the end of 66 days.

The vessel containing oil, Inipol and the Alyeska ballast water biomass exhibited an oxygen uptake curve that was almost superimposable on the non-supplemented curve. Thus, in the closed environment of the respirometric vessel, no enhancement by an external source of enriched organisms was detected.

Microbial Growth Data

Growth data indicate significant increase of growth of the indigenous oil degrading microbiota (increase of 4 to 6 orders of magnitude) at the end of 6 week incubation period. Comparisons of the bacterial colony counts on marine agar plates, providing microbial concentration of heterotrophic population with those on oil agar plates characterizing the growth of hydrocarbon degraders at weekly intervals, indicate a significant increase of the hydrocarbon utilizing bacteria over the first 4 weeks of incubation in the respirometric reactors in contrast to a much lower increase of the heterotrophic population for the same period. The total heterotrophic microbial count leveled off after the first three weeks of incubation with a total increase of 2-3 orders of magnitude, whereas the hydrocarbon utilizing indigenous cell count leveled off after 6 weeks of incubation.

Analytical Data

Figure 4 illustrates a comparison of the GC/FID scans of alkane hydrocarbons in culture samples from respirometric vessels containing 1,000 mg/L oil + Inipol, taken at the start, 6 weeks and 30 weeks of incubation, respectively. These scans demonstrate almost complete utilization of the alkane hydrocarbons in these experimental systems at the end of 6 weeks of incubation. GC/FID scans of alkane hydrocarbons at the end of 6 and 30 weeks of incubation in experimental flasks containing Alyeska ballast water sludge biomass enrichment and in control flasks with Aniline + oil + Inipol also indicate complete aliphatic hydrocarbon utilization after 6 weeks of incubation.

Results based on the GC/MS chromatogram scans demonstrate significant biodegradation of the PAH constituents of the weathered crude oil in experimental respirometric vessels containing 1,000, 300, and 100 mg/L concentrations of oil and 5 percent concentration of Inipol based on oil weight in experimental Alyeska biomass supplement vessels and in the control systems.

Figures 5 through 7 graphically summarize the biodegradation data for the aliphatic hydrocarbons in 1,000 mg/L oil + Inipol respirometric vessels, 1,000 mg/L oil + Inipol + Alyeska ballast biomass supplement vessels and in the toxicity control reactor (1,000 mg/L oil + Inipol + aniline) by relating the initial concentration of these alkanes to those present in cultures after 6 weeks of incubation. Figure 8 compares biodegradation data for the alkanes in 100, 300, and 1,000 mg/L oil + Inipol flasks for 0, 6 and 30 weeks of incubation.

Biodegradation data for PAH hydrocarbon constituents of oil in respirometric vessels containing 1,000, 300 and 100 mg/L oil + Inipol after 0, 6 and 40 weeks of incubation are graphically summarized in Figure 9.

Control experiments using the respirometric approach incorporating the above three oil concentrations without the Inipol EAP 22 nutrient provided evidence of insignificant levels of bioactivity of the indigenous seawater and beach microbiota.

Percent recovery data of surrogate, o-terphenyl from the experimental and control respirometric flask samples and of the matrix spike of the alkanes, n-C15, n-C20 and n-C28 from the naturally weathered crude oil indicate that the percent recovery falls within the range of established QC limit range (60-140 percent). Percent recovery data of the surrogates, naphthalene, acenaphthene and chrysene from experimental and control flask samples and of the surrogates, acenaphthene and pyrene from the naturally weathered crude oil and seawater samples were also shown to be within the established QC limit range. The above percent recovery values for the initial and 6-week samples in the established QC limit range suggest that the analytical data for the alkane and aromatic hydrocarbons have been generated with a good QA/QC data analysis.

FLASK MICROCOSMS

Data from flask microcosms are those based on results obtained by analyses of culture samples for the alkane hydrocarbon and PAH constituents on the Alaskan weathered crude oil at the initiation of the experiment and after six weeks of incubation in shaker flasks.

Results based on GC/FID scans and GC/MS analysis data for the alkane hydrocarbon and PAH constituents of weathered oil in the experimental and control systems under rotary agitation demonstrate significant biodegradation of the PAH constituents in culture media and almost complete utilization of alkane hydrocarbon constituents in presence of 5 percent of Inipol of oil weight after 6 weeks of incubation. Control experiments without Inipol fertilizer provided data which demonstrate insignificant biodegradative activity of the alkane hydrocarbon and PAH hydrocarbon constituents of oil.

Figure 10 illustrates a comparison of the GC/FID scans of alkane hydrocarbons in culture samples from shaker flask microcosms containing 10,000 mg/L oil + Inipol, taken at the start and after 6 weeks of incubation respectively. These scans again demonstrate almost complete biodegradation of

aliphatic hydrocarbons in these experimental systems at the end of 6 weeks of incubation.

Figure 11 summarizes the results of the GC/FID scans of alkane hydrocarbons from flasks containing 10,000 mg/L weathered crude with no nutrients, oil with Inipol, and oil with OECD nutrients. In the no nutrients control, some minor changes in the alkane fractions are evident after 6-weeks incubation. Some of these changes may have been due to biodegradation resulting from background levels of N and P present in the seawater, oil or beach material. The magnitude of the changes, however, was relatively insignificant.

The flask containing the oil plus Inipol exhibited complete removal of all aliphatic components within six weeks. Even the pristane and phytane fractions were reduced to undetectable levels. The flask containing the minimal salts solution (soluble form of N and P) also exhibited complete removal of the straight chain aliphatics. However, there were still measurable amounts of pristane and phytane remaining at six weeks, although the levels were significantly reduced from the no-nutrient controls. These results suggest that Inipol may be enriching for a different type of microbial population from that which is selected by the OECD medium. The Inipol-enriched organisms are not only able to break down straight chain hydrocarbons at a very rapid rate but the branched chain components as well. The OECD-enriched organisms are also able to degrade the branched chain aliphatics, but at a reduced rate or longer lag period.

The GC/MS traces of the aromatic fractions are summarized in Figure 12. In the no-nutrient control (top of figure), several of the components were reduced to undetectable levels after six weeks (note fractions, H, Q, S, and T, corresponding respectively to dibenzothiophene, C3-fluorenes, naphthalene, and C1-naphthalene). The traces from the Inipol and OECD flasks exhibit virtual complete removal of all aromatic fractions after six weeks incubation.

The percent recovery data of the surrogate, o-terphenyl, from the experimental and control shaker flask culture samples and of the surrogate matrix spikes of n-C15, n-C20 and n-C28 alkane hydrocarbons from same flask at zero incubation time and after 6 weeks of incubation were observed to be within the QC limit range for each of the surrogates, thus lending credence to the quality of analytical data generated for alkane hydrocarbons. The percent recovery of the surrogate PAH compounds from culture media was again observed to be within the QC limit ranges for each of these surrogates, demonstrating good QA/QC quality of analytical data for PAH constituents of oil extracted from culture media samples.

CONCLUSIONS

Respirometric and shaker flask microcosm biodegradation data demonstrate a very significant enhancement on biodegradation of alkane and aromatic (PAH) hydrocarbon constituents of oil contaminating the Alaskan beaches of Prince William Sound with the use of the oleophilic fertilizer nutrient, Inipol EAP 22 and the OECD synthetic medium (soluble N and P nutrients).

Rapid and virtually complete biodegradation of all aliphatic and aromatic hydrocarbon components of the weathered crude oil has unequivocally been demonstrated in the closed laboratory environment of the respirometric vessels and flask microcosms.

Almost complete disappearance of these hydrocarbon components occurred within six weeks with some traces of PAH hydrocarbons remaining in the culture systems.

GC/FID chromatographic scans and GC/MS analytical data for the alkanes and PAH hydrocarbons in culture system samples taken after six weeks of incubation indicate complete losses due to biodegradation of these components of the weathered crude oil.

The oxygen uptake in respirometric vessels started after only a 1.5-day lag period, indicating a very active hydrocarbon-utilizing potential of the indigenous seawater and beach sand microbiota of Prince William Sound.

The different microbial populations enriched by the two types of fertilizers suggest that perhaps a combination of Inipol EAP22 and a water soluble source of nutrients may ultimately be the appropriate manner of stimulating rapid bioremediation of crude oil contaminating the Alaskan beaches.

Results from the Alyeska ballast biomass environments suggests that enhancement with external sources of microbial populations would not likely occur and massive inoculum may not be warranted, at least in the Alaskan bioremediation effort.

GC/FID and GC/MS chromatographic scans at 1-week intervals would have provided valuable insight on the rates of disappearance of the individual alkane and aromatic hydrocarbon components of oil. Future experimentation should incorporate more frequent sampling for each analysis.

No inhibitory effects of crude oil at the concentrations of 100, 300, 1,000, 3,000, and 10,000 mg/L in culture systems were observed on both the indigenous biomass and on their biodegradation activities on readily biodegradable or biogenic substrate.

Analytical respirometry was shown to be a valuable experimental approach for testing biodegradability of the hydrocarbon constituents of crude oil contaminating the marine environment and for testing the hydrocarbon biodegradation potential of the indigenous seawater and beach sand microbial consortium in the oil contaminated areas.

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TABLE 1. EXPERIMENTAL DESIGN FOR RESPIROMETRIC STUDIES

Reaction Vessels	Oil Conc., (mg/L)	Intipol Conc. (mg/L)	Alkyssa Ballast (mL)	Beach Sand (g/L)	Seawater (mL)	Aerating (mg/L)
V1, V1R	1,000	50	-	2	1,000	-
V2, V2R	300	15	-	2	1,000	-
V3, V3R	100	5	-	2	1,000	-
V4, V4R	1,000	50	10	2	1,000	-
C1	-	50	-	2	1,000	-
C2	-	-	-	2	1,000	-
C3	1,000	50	-	2	1,000	100
C4	-	50	-	2	1,000	100
C5	1,000	-	-	-	1,000	-
C6	1,000	-	-	2	1,000	-
C7	1,000	50	-	-	-	-

V = Vessel
R = Replicate
C = Control

TABLE 2. EXPERIMENTAL DESIGN OF FLASK MICROCOSMS

Flask	Oil Conc. (mg/L)	Intipol Conc. (mg/L)	OECD	Alkyssa Ballast (mL)	Beach Sand (g)	Sea-water (mL)	Aerating (mg/L)
F1, F1R	10,000	500	-	-	10 U*	1,000	-
F2, F2R	10,000	500	-	-	20 U	1,000	-
F3, F3R	10,000	-	-	-	20 U	1,000	-
F4, F4R	10,000	-	-	-	20 U	1,000	-
F5, F5R	3,000	150	-	-	20 U	1,000	-
F6, F6R	1,000	50	-	-	20 U	1,000	-
F7, F7R	oily sand	2.5	-	-	5 P**	1,000	-
F8, F8R	-	9.0	-	-	10 P	1,000	-
F9, F9R	-	7.5	-	-	15 P	1,000	-
C1	-	500	-	-	20 U	1,000	-
C2	-	-	-	-	20 U	1,000	-
C3	10,000	500	-	-	20 U	1,000	100
C4	-	-	-	-	20 U	1,000	100
C5	-	500	-	-	20 U	1,000	100
C6	-	-	-	-	20 U	1,000	100
C7	-	-	-	-	20 U	1,000	-
C8	-	-	-	-	20 U	1,000	-
C9	10,000	-	-	-	20 U	1,000	-
C10	10,000	-	-	-	20 U	1,000	-
C11	oily sand	7.5	-	-	15 P	1,000	-
C12	oily sand	-	-	-	15 P	1,000	-

F = Flask
R = Replicate
C = Control
U = Unpolluted
P = Polluted beach sand

TABLE 3. ALIPHATIC CONSTITUENTS OF ALASKAN PRUDHOE BAY CRUDE OIL BY GC/FID ANALYSIS

Alkane Hydrocarbons	Concentration, ug/g (ppm)	
	Naturally weathered Alaskan Crude Oil	Artificially weathered Alaskan Crude Oil
C 8	56.4	d
C 9	50.6	69.0
C 10	83.9	411
C 11	186	819
C 12	294	1150
C 13	370	1180
C 14	605	1410
C 15	812	984
C 16	644	1010
C 17	675	729
PRISTANE	620	585
C 18	732	896
PHYTANE	608	434
C 19	517	708
C 20	558	827
C 21	331	574
C 22	340	479
C 23	229	590
C 24	252	721
C 25	130	480
C 26	192	622
C 28	111	379
C 30	64.6	226
C 32	33.9	146
C 34	<2.5	<2.5
C 36	<2.5	<2.5
C 38	<2.5	<2.5

TABLE 4. AROMATIC CONSTITUENTS OF ALASKAN PRUDHOE BAY CRUDE OIL BY GC/MS ANALYSIS

Polycyclic Aromatic Hydrocarbons	Concentration, ug/g (ppm)	
	Naturally weathered Alaskan Oil	Artificially weathered Alaskan Oil
Acenaphthene	7.48	23.1
Acenaphthylene	8.76	43.6
Benzo(a)Pyrene	< 5	5.26
Benzo(b)Fluoranthene/Benzo(k)Fluoranthene	< 5	< 5
Benzo(g,h,i)Perylene	< 5	13.9
Chrysene/Benzo(a)Anthracene	7.43	15.5
C1-Chrysenes	7.26	15.5
C2-Chrysenes	< 0.5	< 0.5
C3-Chrysenes	< 0.5	2.46
C4-Chrysenes	< 0.5	< 0.5
Dibenz(a,h)Anthracene	< 10	< 10
Dibenzothiophene	24.0	83.4
C1-Dibenzothiophenes	60.9	153
C2-Dibenzothiophenes	58.8	133
C3-Dibenzothiophenes	32.8	62.1
Fluoranthene	4.56	4.98
C1-Fluoranthenes/pyrenes	< 0.5	< 0.5
Fluorene	18.8	61.9
C1-Fluorenes	11.0	23.1
C2-Fluorenes	60.9	110
C3-Fluorenes	54.0	97.8
Indeno(1,2,3-cd)Pyrene	< 5	< 5
Naphthalene	18.1	187
C1-Naphthalenes	62.1	347
C2-Naphthalenes	124	410
C3-Naphthalenes	69.5	207
C4-Naphthalenes	31.9	96.5
Phenanthrene/anthracene	20.8	174
C1-Phenanthrenes/anthracenes	39.0	93.2
C2-Phenanthrenes/anthracenes	36.5	81.9
C3-Phenanthrenes/anthracenes	21.0	47.9
C4-Phenanthrenes/anthracenes	3.79	7.33
Pyrene	2.38	4.58

Oxygen Uptake on Weathered Crude Oil

— OIL + INIPOL INIPOL

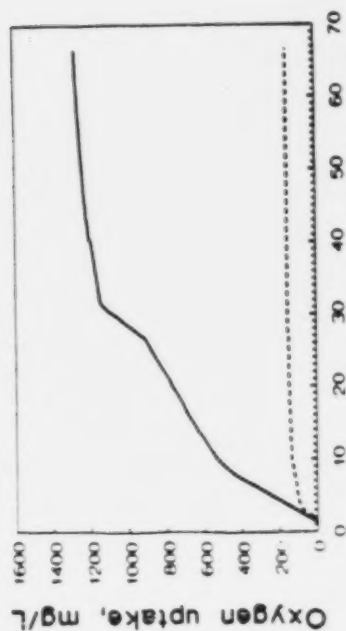


FIGURE 1. CUMULATIVE OXYGEN UPTAKE IN RESPIROMETRIC FLASK WITH 1.000 ml/L OF WEATHERED CRUDE OIL AND INIPOL (2022).

Oxygen Uptake on Weathered Crude Oil

— INOCULUM CONTROL (NO OIL OR INIPOL) — PHYSICAL/CHEMICAL CONTROL (OIL ALONE)

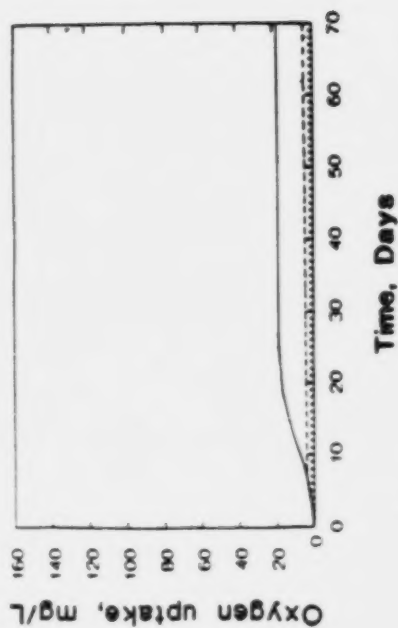


FIGURE 2. CUMULATIVE OXYGEN UPTAKE IN INOCULUM AND SUBSTRATE CONTROL RESPIROMETRIC FLASKS.

Oxygen Uptake on Weathered Crude Oil

— NO NUTRIENT CONTROL (OIL WITH NO NUTRIENT) SUBSTRATE/NUTRIENT CONTROL (OIL AND NUTRIENT ALONE)

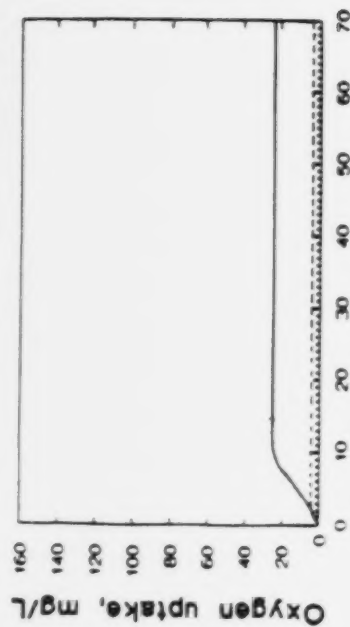


FIGURE 3. CUMULATIVE OXYGEN UPTAKE IN NO NUTRIENT AND SUBSTRATE/NUTRIENT CONTROL RESPIROMETRIC FLASKS.

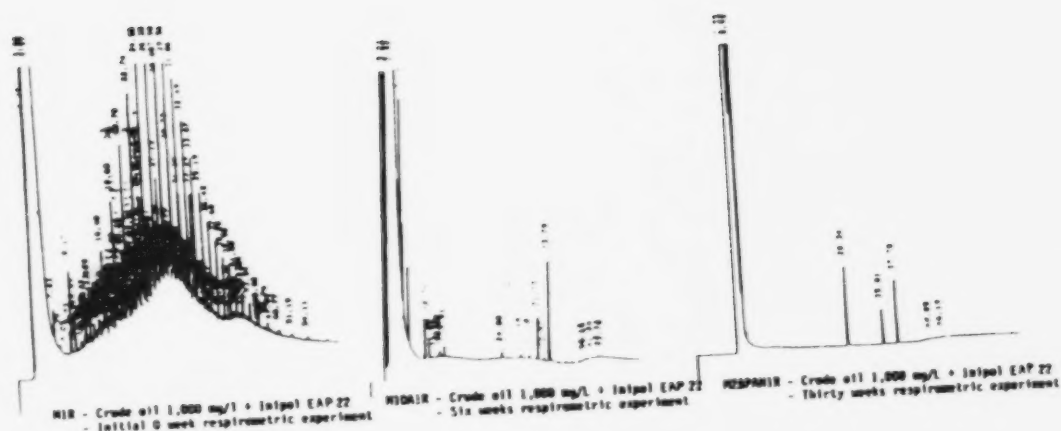


FIGURE 4. COMPARISON OF GC/FID SCANS OF ALKANE HYDROCARBONS IN CULTURE SAMPLES FROM RESPIROMETRIC FLASKS CONTAINING 1,000 MG/L OIL + INIPOL EAP22 AFTER 0, 6 AND 30 WEEKS OF INCUBATION.

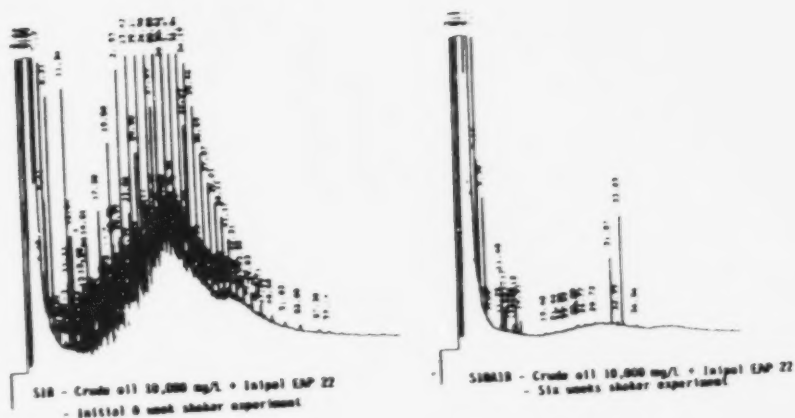


FIGURE 10. COMPARISON OF GC/FID SCANS OF ALKANE HYDROCARBONS IN CULTURE SAMPLES FROM SHAKER FLASKS CONTAINING 10,000 MG/L OF OIL + INIPOL EAP22 AFTER 0 AND 6 WEEKS OF INCUBATION.

BIODEGRADATION OF 1000 mg/L CRUDE OIL IN
PRESENCE OF BALLAST WATER BIOMASS

0 WEEKS 6 WEEKS



Figure 6 Biodegradation of aliphatic hydrocarbons in 1,000 mg/L Alaskan weathered crude oil in

Alkanes

BIODEGRADATION OF ALIPHATIC HYDROCARBONS
IN 1000 mg/L ALASKAN WEATHERED CRUDE OIL

0 WEEKS 6 WEEKS



Figure 5 Biodegradation of aliphatic hydrocarbons in 1,000 mg/L Alaskan weathered crude oil

Alkanes

BIODEGRADATION OF WEATHERED CRUDE OIL IN
THE PRESENCE OF ANILINE

START 6 WEEKS



Figure 7 Biodegradation of aliphatic hydrocarbons in 1,000 mg/L Alaskan weathered crude oil in respirometric flasks containing aniline.

Alkanes

RESPIROMETRIC STUDIES WITH INIPOL

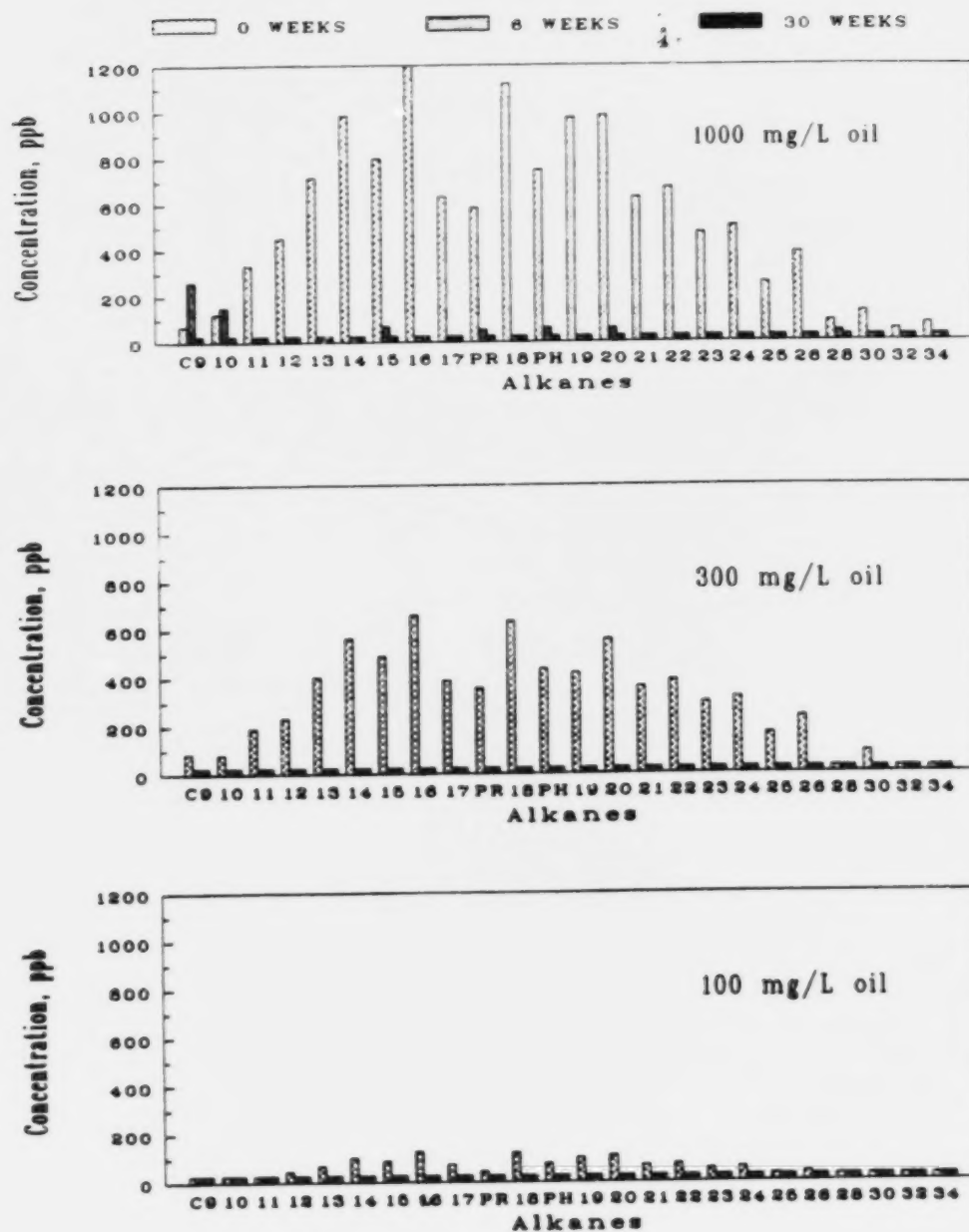
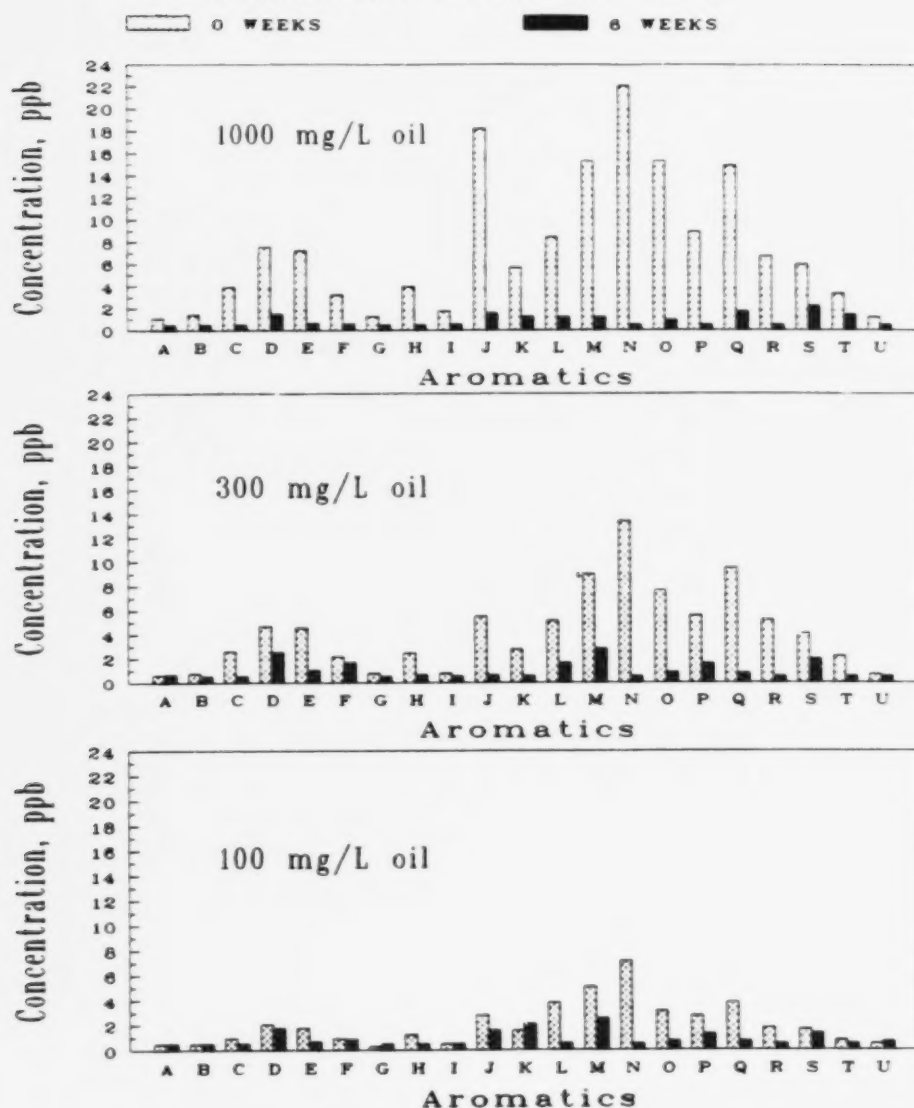


FIGURE 8. COMPARISON OF BIODEGRADATION DATA FOR ALKANE HYDROCARBONS IN RESPIROMETRIC FLASKS CONTAINING 100, 300 AND 1,000 MG/L OIL + INIPOL EAP22 AFTER 0, 6 AND 30 WEEKS OF INCUBATION.

RESPIROMETRIC STUDIES WITH INIPOL



A acenaphthene	H fluorene	O C3-naphthalenes
B acenaphthylene	I C1-fluorenes	P C4-naphthalenes
C dibenzothiophene	J C2-fluorenes	Q phenanthrene/anthracene
D C1-dibenzothiophenes	K C3-fluorenes	R C1-phenanthrenes/anthracenes
E C2-dibenzothiophenes	L naphthalene	S C2-phenanthrenes/anthracenes
F C3-dibenzothiophenes	M C1-naphthalenes	T C3-phenanthrenes/anthracenes
G fluoranthene	N C2-naphthalenes	U pyrene

FIGURE 9. COMPARISON OF BIODEGRADATION DATA FOR AROMATIC HYDROCARBONS IN RESPIROMETRIC FLASKS CONTAINING 100, 300 AND 1,000 MG/L OIL + INIPOL EAP22 AFTER 0, 6 AND 30 WEEKS OF INCUBATION.

DEGRADATION OF ALIPHATICS -- SHAKER FLASK STUDIES

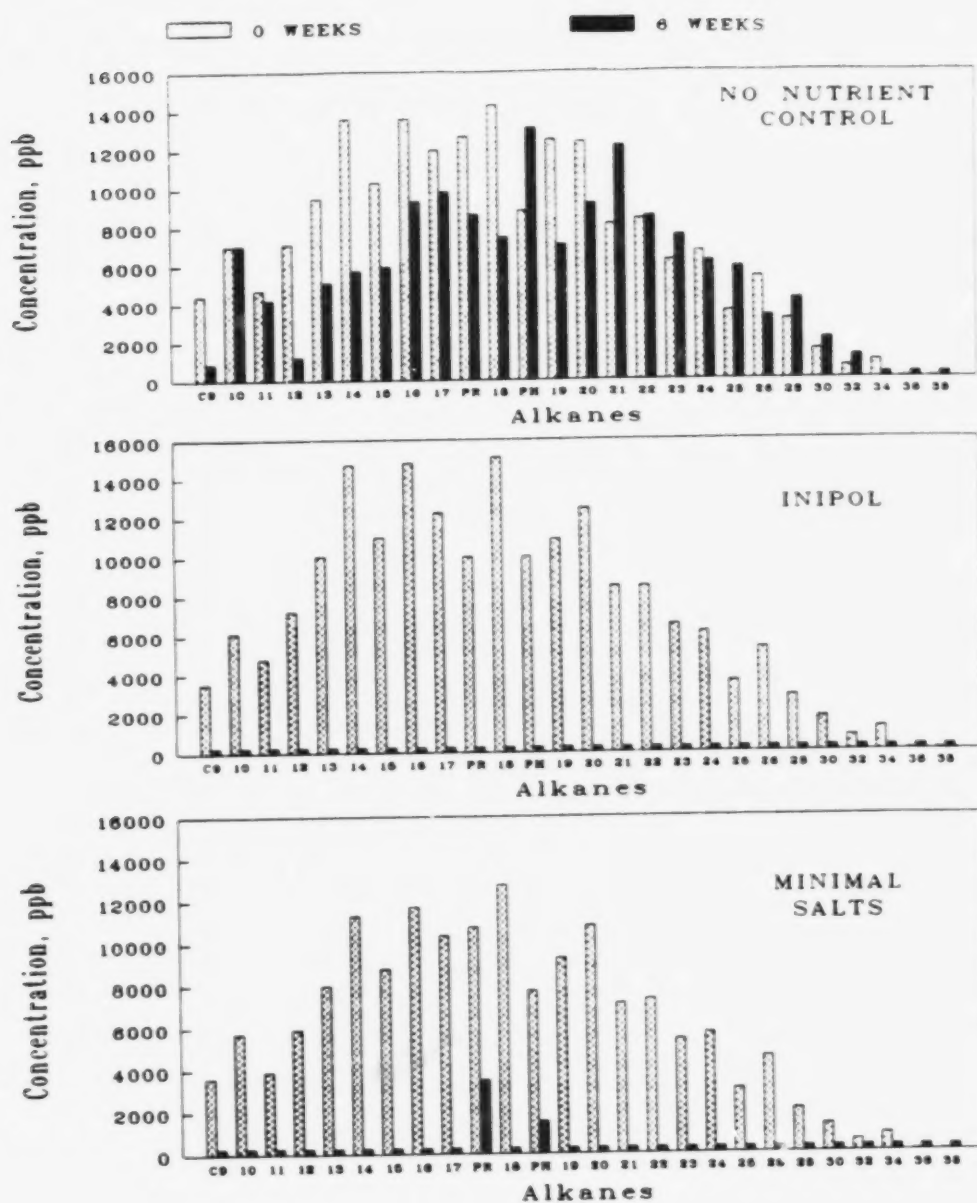


FIGURE 11. COMPARISON OF BIODEGRADATION DATA FOR ALKANE HYDROCARBONS IN SHAKER FLASKS WITH 10,000 MG/L OIL + INIPOL, WITH 10,000 MG/L OIL + MINIMAL SALTS AND IN FLASK WITH NO NUTRIENT.

DEGRADATION OF AROMATICS -- SHAKER FLASK STUDIES

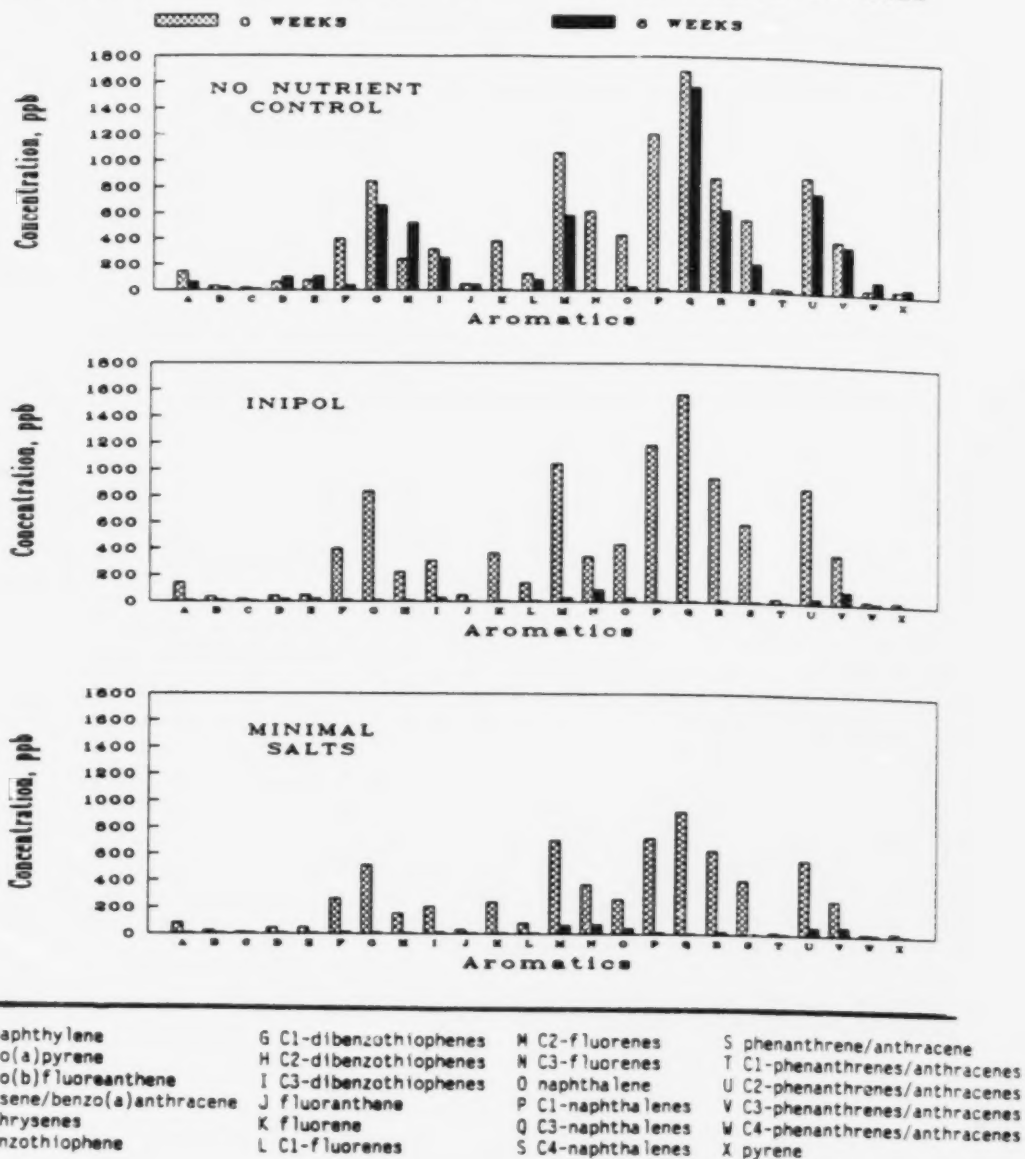


FIGURE 12. COMPARISON OF BIODEGRADATION DATA FOR AROMATIC HYDROCARBONS IN SHAKER FLASKS WITH 10,000 MG/L OIL + INIPOL, WITH 10,000 MG/L OIL + MINIMAL SALTS AND IN FLASK WITH NO NUTRIENT.

BIOLOGICAL TREATMENT OF WASTEWATER CONTAINING
HAZARDOUS ORGANIC COMPOUNDS: 2-ETHOXYETHANOL

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ABSTRACT

Biological treatment is one potential technology for treatment of RCRA-listed wastes containing hazardous organic compounds in concentrations up to 1% (10,000 mg/L), provided that the compounds are not recalcitrant or toxic to the microorganisms in the system. As part of the USEPA's in-house testing program at the Test & Evaluation Facility, biological treatment was evaluated as a treatment technology for 2-ethoxyethanol, a solvent that can occur as the major constituent in RCRA-listed F005 wastes.

Respirometry was used to screen 2-ethoxyethanol for toxicity under aerobic conditions. Toxicity did not occur in the concentration range studied (0 mg/L - 10,000 mg/L), and the data implied that biodegradation occurred.

Pilot-scale activated sludge systems were subsequently used to further evaluate the fate of 2-ethoxyethanol in aerobic systems. The pilot-scale systems were operated at a flow rate of approximately 11 liters per day for a 24-hour hydraulic residence time with a target solids retention time of 10 days. The systems were supplied with a synthetic feed which was spiked with 2-ethoxyethanol, and the concentration of 2-ethoxyethanol was measured in feed, effluent, waste sludge and reactor off-gas samples. At the highest feed concentration studied, the system reduced the 2-ethoxyethanol concentration from 2284 ± 201 mg/L in the feed to 18 ± 17 mg/L in the effluent. No 2-ethoxyethanol was detected in the off-gas or waste mixed liquor samples.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The assessment of biological treatment as a viable treatment technology for 2-ethoxyethanol F005 waste was carried out by University of Cincinnati (UC) project staff at the USEPA Test & Evaluation (T&E) Facility during FY88-89 under EPA Contract No. 68-03-4038. This research was part of Work Assignment No.2-WH21.0 entitled "Hazardous Waste Treatment Technology Assessment". The work assignment covered in-house bench and pilot scale testing as part of a larger treatment technology assessment program funded by the Office of Solid Waste (OSW) through the Hazardous Waste Engineering Research Laboratory (HWERL) and, later, the Risk Reduction Engineering Laboratory (RREL).

Preliminary bench-scale testing was done to screen 2-ethoxyethanol for treatability/biodegradability. In these studies, toxicity due to 2-ethoxyethanol was tested in both aerobic and anaerobic systems at concentrations up to 1% as 2-ethoxyethanol. Oxygen uptake rate was used as the measurement parameter for the aerobic studies. Gas production rate was used as the measurement parameter for the anaerobic studies. Toxicity effects were not noted in the tested concentration range and biodegradation was implied in both cases. The aerobic studies are the topic of this paper. The results of the anaerobic studies have been discussed elsewhere(2).

Before biodegradation could be confirmed, a reliable analytical method was required for 2-ethoxyethanol. Poor purging efficiencies required the use of direct injection for introduction of the sample into the gas chromatograph. SW-846 Method 8015 (GC/FID method for nonhalogenated volatile organics - see (1)) was modified to use a column capable of separating trace solvents in aqueous solutions (Supelco Carbowax B/3% SP1500, 80/120 mesh packing or equivalent).

While the analytical method for 2-ethoxyethanol in aqueous solutions was being identified, start-up of two existing activated sludge pilot plants was initiated. After method QA/validation studies were performed, monitoring of the feed and effluent to the two pilot plants was begun. Data from the pilot plant studies are presented and discussed following a brief discussion of the aerobic bench-scale respirometry studies.

RESPIROMETRY STUDIES

A Tech-Line respirometer was used to study the toxicity effects of 2-ethoxyethanol concentration on the oxygen uptake rate of an activated sludge culture. A schematic diagram of the apparatus is shown in Figure 1. The respirometer includes two 4-liter aeration chambers in a single water jacket tank. The seed source was unacclimated activated sludge from a pilot plant at the T&E Facility which treats screened raw wastewater from the Cincinnati Metropolitan Sewer District. Neat 2-ethoxyethanol was obtained as purified grade liquid (Cellosolve) from Fisher Scientific Company. Oxygen uptake rate was measured in milliliters of oxygen per liter of activated sludge per hour (mL/L/hr).

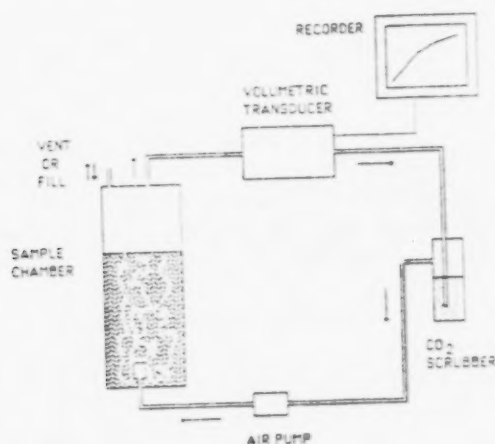


Figure 1. Respirometry Experimental Apparatus

Two types of tests were performed. One type was the Cumulative Toxicity Test recommended by the manufacturer of the respirometer(3). In the first part of this test, a readily degradable carbon source was supplied to both the test and blank cells and 2-ethoxyethanol was spiked into the test cell cumulatively. In the second part, the maximum amount of test compound was added immediately after the background uptake rate had been measured. In analyzing the data, a drop in oxygen uptake rate in the test cell as compared to the rate in the blank cell indicates toxicity. An increase implies biodegradation of the test compound. The results for the 2-ethoxyethanol test are shown in Table 1. Once 2-ethoxyethanol was spiked into the test cell, the oxygen uptake rate in the test cell was always greater than in the blank cell. The rate of uptake declines with time, however, in both cells in the first part of the experiment as the readily degradable carbon source and nutrient supplements are consumed. There appears to be a shift in the relative difference between the uptake rates (4.1 to 1.8 mL/L/hr) after a total of 2320 mg/L was added to the

test cell. However, this phenomenon is more likely due to some factor other than the test compound concentration since in the second part of the experiment, the rates again showed a 4.0 mL/L/hr increase for the maximum 2-ethoxyethanol concentration of 9300 mg/L. No toxicity was observed.

TABLE 1. RESPIROMETRIC CUMULATIVE TOXICITY TEST RESULTS FOR 2-ETHOXYETHANOL (2-E)

2-E Added (mg/L)	Cumulative 2-E (mg/L)	30 min Net Oxygen Uptake Rate (mL/L/hr)		
		Test	Blank	Increase
0	0	14.5	14.7	- 0.2
580	580	16.5	9.7	6.8
580	1160	12.2*	8.1	4.1
1160	2320	10.2	6.1	4.1
2320	4640	7.3	5.5	1.8
4650	9290	6.9	5.4	1.5
9300	18590	6.2	4.5	1.7
0	0	13.2	14.0	- 0.8
9300	9300	12.1	8.1	4.0

* Oxygen uptake rate decreases with time and increasing 2-ethoxyethanol concentration, but it is always greater for the test cell than the blank. If significant inhibition were occurring in the concentration range tested, the oxygen uptake rate in the test cell would be less than the blank.

The second type of test supported this observation. In these tests, no carbon source or feed chemicals other than 2-ethoxyethanol (in the test cell only) were added to the activated sludge culture. Different concentrations of 2-ethoxyethanol were spiked in the range from 23 - 1160 mg/L. Each concentration was tested in a separate experiment on a different day using a fresh sample of activated sludge. The initial oxygen uptake rate for both the spiked and unspiked cultures was measured at each concentration of 2-ethoxyethanol. These data are presented in Table 2. Note that, once again, the oxygen uptake rate in the spiked cell is consistently greater than in the unspiked cell, indicating that the 2-ethoxyethanol is not toxic at these concentrations. This also implies that 2-ethoxyethanol is degradable. The use of different samples of activated sludge is the most likely source of the variability in the data in this set of experiments.

The bench-scale respirometry batch experiments were useful toxicity screening procedures. Since no toxicity was observed in the range tested (0-10,000 mg/L), continuous pilot-scale testing at 2-ethoxyethanol concentrations of 5000 mg/L and 10,000 mg/L

was originally proposed. During the acclimation phase, operation at 5000 mg/L resulted in severe operational problems (bulking and the production of slimy exocellular polysaccharides). It was hypothesized these problems were due to oxygen transport limitations (relative to available carbon substrate) in the microbiological floc resulting in the predominance of bulking organisms and the formation of polysaccharide storage products. The target test concentrations were subsequently reduced to 500 mg/L and 2500 mg/L to alleviate this problem.

TABLE 2. RESPIROMETRIC TOXICITY SCREENING STUDIES: EFFECT OF 2-ETHOXYETHANOL CONCENTRATION ON OXYGEN UPTAKE RATE

		Initial Oxygen Uptake Rate (mL/L/hr)		
Amount 2-E Spiked (mL)	(mg/L)	Spiked	Unspiked	Difference
0.1	23	16.3	8.8	7.6
0.1	23	19.7	12.2	7.5
0.1	23	12.8	7.3	5.4
0.2	46	21.8	8.2	13.6
0.3	70	15.0	8.8	6.2
0.5	116	30.0	12.5	17.5
1.0	232	14.7	5.4	9.3
1.0	232	26.2	10.0	16.2
1.0	232	31.3	9.8	21.5
1.5	349	18.8	8.9	9.9
2.0	465	30.0	7.4	22.6
3.0	698	27.5	10.0	17.5
5.0	1160	21.1	8.0	13.1

ACTIVATED SLUDGE PILOT PLANT STUDIES

DESIGN OF ACTIVATED SLUDGE PILOT PLANTS

Two existing activated sludge pilot plants were used for this portion of the study. See Figure 2. A synthetic feed was chosen over the primary effluent available at the T&E Facility in order to reduce input variability and to facilitate consistent operation of the pilot plants. The basic formula was derived from a mixture described by Kincannon and Stover(4). 2-Ethoxyethanol served as the primary carbon source, eliminating glucose and glutamic acid. At high 2-ethoxyethanol concentrations, the formula required nitrogen and phosphorus supplementation in order to keep the COD:TKN:P ratio at approximately 150:5:1. Feed for each pilot plant was prepared fresh daily from neat reagent grade chemicals

and was stored in a refrigerator at 4 °C as it was pumped to the appropriate pilot plant aeration basin. Samples were collected from each feed carboy just before the carboy was attached to the system.

Effluent from each system was continuously composited in a refrigerated carboy except when the flow was diverted for collection of 2-ethoxyethanol samples one time per day. The 2-ethoxyethanol samples were collected in 40-mL vials with teflon-lined septa. The daily composite samples were used for all other analyses.

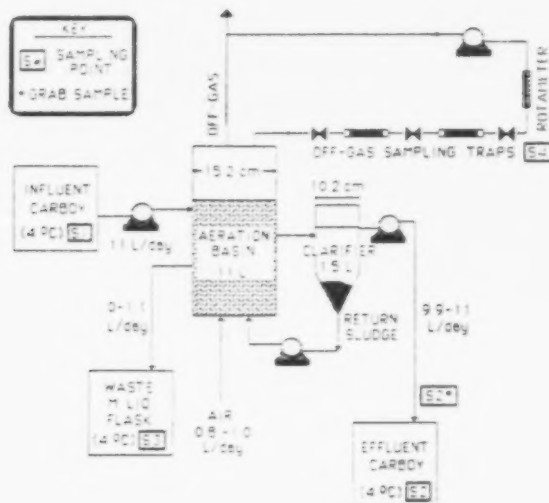


Figure 2. Activated Sludge Pilot Plant Experimental Apparatus

Solids were wasted directly from the aeration basins. Peristaltic pumps were used with timers to deliver the appropriate wasting flowrates, while providing a high enough velocity to avoid clogging. Wastes were composited daily by pumping directly to refrigerated flasks. The appropriate waste flowrate for control of each system was calculated and set daily based on mixed liquor and effluent volatile suspended solids. Samples for all waste mixed liquor analyses were collected from the composites in the refrigerated flasks.

The aeration basin off-gas was sampled using the charcoal sorbent tubes specified in NIOSH Method 1403 (5). The maximum flowrate specified in the method, 0.05 L/min, was used for a total of 2 hours per sample, or a maximum volume of 6 L. A second tube

was placed in series with the sample tube to quantitate any breakthrough of 2-ethoxyethanol.

PROCESS MONITORING DATA

Tables 3 and 4 summarize the routine process monitoring data for solids retention time (SRT), total and volatile suspended solids (TSS/VSS), dissolved organic carbon (DOC) and 2-ethoxyethanol (2-E) for target test concentrations of 500 mg/L and 2500 mg/L. Mean values with standard deviations for the acclimation phase (three SRTs just before the test phase) and for the four-day test phase itself are presented.

Because 2-ethoxyethanol served as the primary carbon source in the feed, the amount of biomass produced in the aeration basin is proportional to the 2-ethoxyethanol concentration. The large standard deviations for the acclimation phases are due both to expected fluctuations inherent in the acclimation process and to system upsets resulting from operational problems (temperature fluctuations and plugging lines). The DOC removals were approximately 70% with the exception of the test phase for the second concentration in which they averaged 86% as system operation improved. The 2-ethoxyethanol removals were 80 - 90% with the exception of the test phase for the second concentration in which they reflected the improvement in system operation and averaged 99%. Normally a longer recovery period after a system

TABLE 3. PILOT PLANT PROCESS MONITORING DATA FOR
500 MG/L 2-E SYSTEM

Parameter	Acclimation	During Test
Average SRT, days	10.2	11.4
Aeration basin TSS, mg/L	650 $\pm$ 233	870 $\pm$ 60
Aeration basin VSS, mg/L	571 $\pm$ 228	793 $\pm$ 59
Effluent TSS, mg/L	12 $\pm$ 9	5 $\pm$ 2
Effluent VSS, mg/L	8 $\pm$ 6	3 $\pm$ 2
Influent DOC, mg/L	320 $\pm$ 10	305 $\pm$ 3
Effluent DOC, mg/L	91 $\pm$ 40	94 $\pm$ 5
% DOC Removal	71 %	69 %
Influent 2-E, mg/L	479 $\pm$ 18	495 $\pm$ 40
Effluent 2-E, mg/L	33 $\pm$ 21	92 $\pm$ 18
% 2-E Removal	93 %	81 %

TABLE 4. PILOT PLANT PROCESS MONITORING DATA FOR
2500 MG/L 2-E SYSTEM

Parameter	Acclimation	During Test
Average SRT, days	8.4	8.8
Aeration basin TSS, mg/L	3104 $\pm$ 2136	2065 $\pm$ 156
Aeration basin VSS, mg/L	2202 $\pm$ 1501	1494 $\pm$ 167
Effluent TSS, mg/L	77 $\pm$ 68	41 $\pm$ 4
Effluent VSS, mg/L	52 $\pm$ 34	29 $\pm$ 5
Influent DOC, mg/L	1540 $\pm$ 50	1485 $\pm$ 84
Effluent DOC, mg/L	481 $\pm$ 207	208 $\pm$ 65
% DOC Removal	68 %	86 %
Influent 2-E, mg/L	2255 $\pm$ 290	2284 $\pm$ 201
Effluent 2-E, mg/L	345 $\pm$ 380	18 $\pm$ 17
% 2-E Removal	85 %	99 %

upset would be desirable prior to test phase data collection, but initiation of the test phase was constrained by project deadlines. The amount of 2-ethoxyethanol measured in the effluents from both systems shortly after seeding was under the detection limit of 10 mg/L. The 2500 mg/L system returned to this degree of removal for the last three of the four test phase days, resulting in better removals than in the 500 mg/L system.

MASS BALANCE CALCULATIONS

During the test phase for each concentration, all streams entering and leaving the system were analyzed for 2-ethoxyethanol so a mass balance could be used to examine the fate of 2-ethoxyethanol in the system and to indirectly estimate the amount of removal attributable to biodegradation. These streams included the aeration basin off-gases and wasted mixed liquor in addition to the influent and effluent.

Aeration basin off-gases were sampled by passing 6 L of gas through charcoal sorbent tubes. The charcoal was then eluted according to NIOSH Method 1403 (5) with methylene chloride containing 5% v/v methanol and an internal standard. The eluent was analyzed using a gas chromatograph with a flame ionization detector. The detection limit for this method was 0.02 mg 2-ethoxyethanol per tube (or 6 L gas). No 2-ethoxyethanol was found

in detectable quantities in the gas samples. The detection limit was used for purposes of mass balance calculations.

Wasted mixed liquor samples were handled two different ways, depending on the mixed liquor suspended solids concentration of the sample. For the system which was fed 500 mg/L 2-ethoxyethanol, only the filtrate was analyzed because the mixed liquor suspended solids concentration was low. No 2-ethoxyethanol was found in detectable quantities in this sample, and the detection limit for the direct injection method discussed earlier, 10 mg/L, was used for purposes of mass balance calculations. For the system which was fed 2500 mg/L 2-ethoxyethanol, the suspended solids concentration was high enough that it was necessary to analyze the solids in addition to the filtrate. The solids from 50 mL of sample were collected on filter paper and extracted with 50 mL of methanol. The extracts were then analyzed using the direct injection method. No 2-ethoxyethanol was detected in the filtrate or extract. For the solids, the estimated detection limit based on recoveries of 2-ethoxyethanol from methanol was 56.8 mg/L. For mass balance calculation purposes, the total amount of 2-ethoxyethanol which could have been present in the mixed liquor sample without being detected was estimated as the sum of the filtrate extract detection limits, i.e., 66.8 mg/L.

The mass balances around each system for target 2-ethoxyethanol concentrations of 500 and 2500 mg/L are illustrated in Figures 3 and 4, respectively. The mass flowrates were calculated from the measured 2-ethoxyethanol concentration (mg/L) multiplied by the measured flowrate (L/min) for the given sample stream. The term "apparent biodegradation" represents the difference between the mass flowrate of 2-ethoxyethanol into the system via the influent and out of the system via the effluent, off-gases and wasted mixed liquor streams. Although this term is primarily due to biodegradation, it does not strictly represent only biodegradation because it also incorporates any errors inherent in sampling and analysis as well as possible losses due to chemical reaction. The apparent biodegradation at 500 mg/L was >80.9%. At 2500 mg/L, it was >98.8%. These values represent conservative estimates because effluent concentrations in both systems were elevated due to operational upsets in the systems discussed earlier.

CONCLUSIONS

Respirometry and the anaerobic toxicity assay were used to screen 2-ethoxyethanol for toxicity. Toxicity did not occur in the concentration range studied (0 - 10,000 mg/L) and biodegradation was implied. In pilot-scale testing of 2-ethoxyethanol, the activated sludge system reduced the feed concentration from 495 ± 40 to 92 ± 18 mg/L and from 2284 ± 201 mg/L to 18 ± 17 mg/L. No 2-ethoxyethanol was detected in the off-gas samples or in the wasted mixed liquor samples.

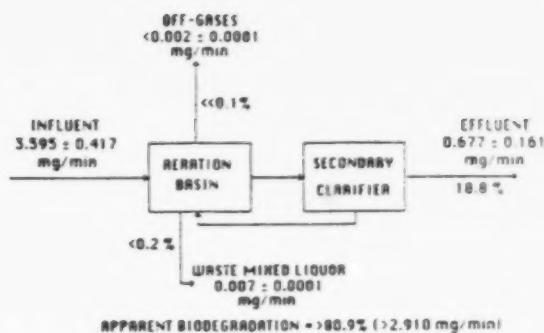


Figure 3. Mass Balance for
500 mg/L System

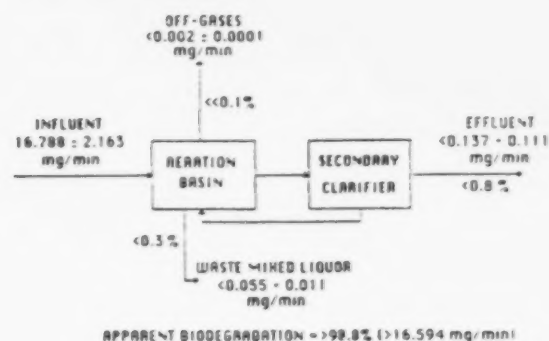


Figure 4. Mass Balance for
2500 mg/L System

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BENCH-SCALE BIODEGRADATION STUDIES WITH ORGANIC POLLUTANTS
USING A WHITE ROT FUNGUS

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ABSTRACT

An array of naturally occurring and xenobiotic waste materials have been shown to be degraded by the white rot fungus, Phanerochaete chrysosporium. The ability of this fungus to degrade the wide spectrum of organic substrates is attributable in part to the production of extracellular enzymes commonly called ligninases, for their ability to degrade lignin. The mixture of ligninases produced by P. chrysosporium is composed of 10-15 peroxidases that appear among the strongest biological oxidants known. The production of these enzymes occurs in a secondary metabolic state that is supported by the cometabolism of more easily degraded carbon substrates. The application of this fungus to treat liquid phase wastes has been designed to use a rotating biological contactor. The MyCoR process has been demonstrated for the treatment of pulp and paper industry waste water through the decolorization and degradation of color-producing bodies and contaminating chlorinated compounds. Bench scale studies have advanced the general operation of this reactor but scale up has not been undertaken. This paper describes bench scale studies devoted to a systematic investigation of operational factors and their sensitivity for use at pilot scale.

BACKGROUND

White rot fungi are found throughout the Northern Hemisphere and are known for their ability to degrade wood components (cellulose and lignin). Phanerochaete chrysosporium, a white rot fungus, is a species that has been selected for intense investigation due to its superior ability to degrade lignin (1).

Lignin is a biogenic, high molecular weight polymer, composed of a series of substituted phenyl propanoic units and is resistant to

biodegradation (2). The biological polymerization process forms lignin polymers that are disperse and non-homogeneous in composition (2). For the fungus to break down the highly variable lignin polymer structure, enzymes of low specificity and low selectivity are required. P. chrysosporium is endowed with such a complement of enzymes that enable it to degrade lignin. The fungal enzyme system is extracellular and is composed of a series of enzymes called ligninases. Ligninases are peroxidases that utilize hydrogen peroxide to oxidize organic substrates. Due to the low specificity of the ligninase enzymes systems, P. chrysosporium has been tested for its ability to degrade a variety of waste components: chlorinated phenols (3), eg. pentachlorophenol (4,5), polyaromatic hydrocarbons (6,7), polychlorinated biphenyls (8), polymeric dyes (9), and pesticides (10).

The powerful extracellular enzyme system is induced in response to specific nutrient deprivation in nature. Proper conditions for the induction of ligninase production can be simulated in the laboratory and reactors without lignin as a substrate (11,12). The metabolic phase responsible for this shift in activity is distinct from the primary growth of the organism and is referred to as a secondary metabolic phase (13).

One waste treatment application of white rot fungi is based on the use of a liquid bioreactor configured as a rotating biological contactor, the MyCoR process (14,15). Other reactor configurations have been investigated (16). The MyCoR process has been demonstrated at bench scale for the treatment of paper and pulp industry wastewater. The color-producing bodies and contaminating chlorinated compounds characteristic of these effluents are removed by the process (15,17). The original work using this fungus to treat these effluents was first published in 1977 (20).

INTRODUCTION

This research program explores the MyCoR process for its potential use as a hazardous waste site cleanup technology. The MyCoR technology has been studied at research scale to establish the proof of concept. To extend this line of development, we have chosen the decolorization of Kraft pulp mill effluent as a means to begin the optimization of operational conditions at the bench-scale. This program addresses issues of application practicality to develop cost-effective and efficient treatment technology.

STUDY DESIGN

All factors were held constant for the operation of a given reactor throughout the growth and secondary metabolic phases of each experiment with the exception of oxygen supply. In selected experiments, growth was initiated under an air atmosphere which was replaced with a pure oxygen supply at 48 hour operation. Variables studied included:

- (1) Air vs increased oxygen concentration
- (2) Glucose concentrations of 1.0%, 0.5%, and 0.1%
- (3) Nitrogen concentrations to support ligninolytic (secondary phase) and non-ligninolytic (primary phase) conditions
- (4) Choice of buffer either 2,2-Dimethyl Succinate (DMS) or Potassium Tartrate (KTar)
- (5) Disk rotational speeds were 1 or 6.5 rpm

MATERIALS & METHODS

WASTEWATER SOURCE

Kraft pulp mill effluent from a post-chlorination, base treatment stage was sampled on a schedule corresponding with the same type wood pulp processing. Periodic samples of 10-50 gallons were collected as needed to maintain a steady source for reactor treatment studies.

REACTOR OPERATION

Stationary cultures of fungus were maintained on a 3% agar (1% malt, 1% glucose), pH 4.5. Cultures were kept both at room temperature and incubated at 34° C.

Bench-scale rotating biological contactors (RBCs) were constructed from plans provided by Dr. T. Joyce, North Carolina State University (16). These reactors were operated in both growth and treatment phases in a constant temperature room at 33-35° C. The pH of the reactor contents was maintained at 4.25-4.7 through daily adjustments to 4.4-4.5 with 1N HCl or NaOH.

Inoculation and development of biofilm in the reactors were conducted in accordance with literature instructions except where changes were investigated as part of the study (14,15). Biofilms were grown both on synthetic media and in the presence of pulp mill effluent supplemented by nutrient and mineral additions. Five to seven days for biofilm growth and treatment acclimation were required before treatment assessment.

REACTOR MAINTENANCE PROCEDURE

Sample collection and pH adjustment was scheduled on at least a daily basis. Removal of liquid and pH adjustment was conducted by means of cannula and a syringe. Sample collection and operational time did not change the initial liquid volume of 2-L per reactor by more than 10% at completion of batch runs. Wet weights of biofilms were measured by upon completion of the reactor batch runs after draining the liquid phase from each RBC.

The gas atmospheres were established by allowing free gas exchange with the ambient atmosphere for air mediated experiments whereas elevated oxygen concentrations were established by sealing the lid of the RBC with tape and

supplying pure oxygen to the reactor. For the supplied oxygen experiments, the headspace of the reactors was aggressively flushed with pure oxygen for 5-15 minutes before the oxygen flowrate was adjusted to a constant rate of 20mL/min.

ANALYTICAL TECHNIQUES

Dissolved oxygen was measured by YSI Model 54A meter with stirring BOD probe YSI model 5720A. Ambient atmospheric oxygen concentration was measured with a Fisher Model 1200 Gas Partitioner. Spectroscopic measurements of UV/Vis were measured with a Beckman Model 25 spectrophotometer. Measurements were made on filtered liquid samples. Wavelengths were chosen to monitor the reduction of substrate concentration throughout the batch treatment periods which ranged from 2 days to 1 week. Due to the heterogeneity of the Kraft pulp mill effluent, a single wavelength was considered inappropriate to measure rates of conversion. The wavelengths of 580 nm (measuring the yellow-orange color region), 450 nm (for humic substance detection), 280 nm (for aromatic structure and lignin fragment detection) were used (19,20). In pulp mill wastes, peak absorbance is at 220 nm. A wide flattened peak is found at 280 nm. The highly concentrated nature of the effluent required dilution for spectrophotometric measurements. A nine percent dilution was found to be in the linear range to calculate a relative percent concentration based on Beer's law at 280 nm. Color was measured as platinum color units (PCU) which is a standard method developed by the paper and pulp mill industry (23).

Treatment capacity was assessed by the total and percent reduction of the representative wavelength absorbances and color units original zero time sample (T0) set to equal 100%. Data for initial experiments were collected by measuring absorbance at 580 nm only. Subsequent experiments showed a strong linear correlation between the visible wavelengths and color units. The regression data for this correlation are as follows:

$$m = 0.000073 \quad b = -0.02183 \quad R^2 = 0.926211 \quad \text{no. observations} = 143.$$

Consecutive treatment results in the same reactor/biofilm were averaged to minimize the biological variability (22). Percent reduction at 280nm represents reduction of substrates related largely to aromatic fractions and not total color. The correlation of color units and absorbance at 280 nm exhibits a large scatter indicating a lack of linear correlation between color and UV absorbance. Absorbances at the 220 nm wavelength fluctuated throughout the treatment study making assessment of these results difficult. Following acclimation, a period of 1 day was considered significant treatment time. More critical evaluation assessed treatments under 24 hours (Table 1).

TABLE 1. REMOVAL MEASUREMENTS BY DIFFERENT MEANS OF DETECTION

		Total Average Removal (%)			
REACTOR CONDITIONS		8 HR		17 HR	
GLUCOSE %	DISK SPEED (rpm)	280 nM	Color Units	280 nM	Color Units
1.0	1	10	39	19	57
1.0	6.5	13	41	23	59
0.5	6.5	11	33	19	55
0.5	1	5 11	27 39	20 21	51 55

Continuous liquid-liquid extraction (EPA Method 3250) followed by GC/MS EPA 8270 for chlorophenols. A Hewlett-Packard GC/MS with HP autosampler and HP software was used for peak integration. For semi-quantitation and preliminary data generation GC/FID was used.

DISCUSSION

GROWTH

No discernible difference in growth or activity was observed in the biofilms inoculated with spores cultivated at room temperature compared to those at 34° C. Sufficient numbers of spores for the inoculation of 2-6 reactors were grown within 10 days at 34° whereas a 2 weeks was required for room temperature growth of spores.

No significant differences were observed in the consecutive treatment performance of biofilms developed in the presence of pulp mill effluent and those developed purely on synthetic media. An initial growth and acclimation period of 1 week was required after start-up in both cases.

Under all conditions of growth and treatment, but not at all times, black and red coloration of the biofilm developed in the form of localized "speckled" areas. Speculation has attributed such coloration to one or more of the manganese dependent ligninase enzymes.

When environments of purified oxygen were established with the initial inoculation of a reactor, a tendency was observed for some of the fungal mass to group into spherical clumps on the discs. This was not observed when biofilm growth was begun under air.

OXYGEN CONCENTRATION

It is known that fungal growth is facilitated by lower oxygen concentrations (23), but that the lignin degrading system of this fungus is positively influenced by increasing the oxygen concentration in the transition between primary and secondary metabolism (24). No discernible difference in treatment was noted when cultures were placed initially under an increased oxygen atmosphere despite the smoother appearance of the biofilm. The cost of oxygen supports the practice of early growth under air for consideration at pilot and field scale.

Invariably with all other parameters held constant, more biomass developed under air than increased oxygen. When treatment failed in a set of reactors under increased oxygen, the fungus grew to a weight comparable to that grown in the presence of air.

Initial acclimation to the pulp mill effluent was found to be slower in the presence of air than in the presence of higher oxygen concentrations. These reactors decolorized dilute effluents comparably. The oxygen assisted reactor systems showed comparable treatment activity for both dilute (≤ 3000 PCU) and concentrated (≥ 4000 PCU) effluents. However, reactors with air atmospheres showed greatly diminished decolorization rates for concentrated pulp mill effluent than the rate observed for the more dilute effluents (Fig. 1).

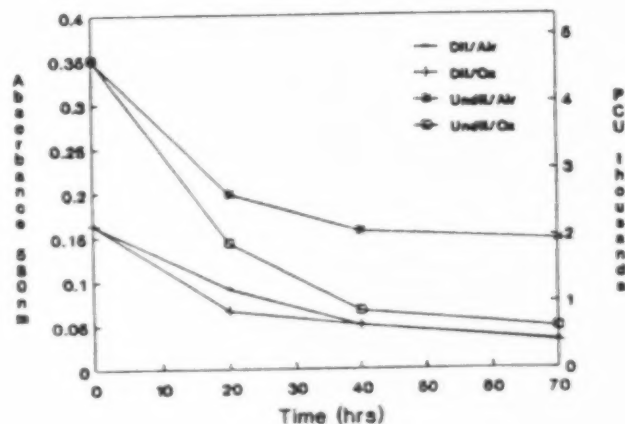


Figure 1. Effect of oxygen on concentration.

In similar studies, Yin et. al. demonstrated the kinetics of color removal by *P. chrysosporium* is concentration dependent with effluents containing ≤ 8000 PCU (22). The effluent concentration used in our studies was 4000-5500 PCU. Hence, oxygen concentration and its availability are determinative factors for the biological treatment of these effluents in RBCs. Therefore, these results suggest strong correlation between oxygen requirements and pulp mill effluent color concentration. The relationships indicated by these observations will be integral to commercial operation of a treatment system of this design.

GLUCOSE

It is known that glucose is used *de novo* to produce hydrogen peroxide from molecular oxygen. This product is used by the ligninases in the oxidative depolymerization of lignin (24). The dual role for glucose in both growth and secondary metabolism is supported by the growth and treatment results described in this study.

The amount of biofilm growth is not directly proportional to glucose concentration. Under increased oxygen concentrations, 0.5% glucose performed treatment as efficiently as 1.0%. See tables 1 and 2. Under air, only with dilute effluent, the activities of the initial acclimation/treatment batch and the second consecutive batch were comparable at the two glucose concentrations. The treatment of later batches were accompanied with a decline in the rate of decolorizing activity at the 0.5% glucose level. However, the extent of decolorization ultimately was maintained by employing longer treatment periods. The decolorization rate was maintained at 1% glucose for dilute effluent feedstocks. An additional factor of carbon source is indicated here in terms of concentration, oxygen and kinetics. A critical concentration between 0.1 and 0.2% glucose has been identified as necessary for decolorization with supplied oxygen (26). Preliminary results show activity at 0.1% yet at a decreased rate.

NITROGEN

Experiments using nitrogen-rich media, conditions that do not induce the lignin degrading secondary metabolic state in non mutant fungal species, throughout the treatment resulted in an interesting "non-active" condition. Physical attachment of color bodies was noted on the biofilm for a period of 1-2 days followed by their release back into the liquid matrix. Substrates monitored at the 280 nm wavelength also displayed this uptake/release phenomenon. This is to be contrasted with conditions of observed "inactivity" where no initial uptake by the fungus is observed and no treatment occurs (Fig. 2). In slower acting systems (i.e. under air), residual attached color from a previous batch is decolorized upon the addition of a new batch of effluent containing a fresh supply of glucose (i.e., H_2O_2).

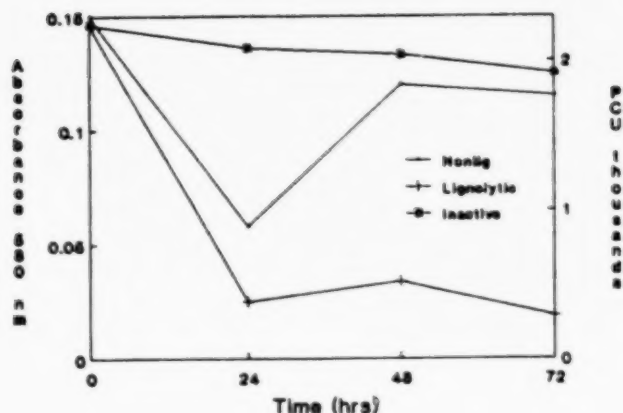


Figure 2. Performance overview.

Physical attachment or adsorption of substrate to the fungal biofilm is primary to initiating subsequent degradation by the fungus. The treatment "inactivity" observed may be an inhibition of this first step. A total removal was based on measurement of the liquid concentrations of color and individual organic substrates. For example trichlorophenol concentrations of 18 ppb in the pulp mill effluent were not detected after treatment even in the case where the desired enzymatic conditions for treatment had not been established. This loss of phenol was attributed to the a great retentive characteristics of the developed non-ligninolytic biofilm.

BUFFER

No difference in growth or treatment extent was observed when potassium tartrate (KTar) was used in the place of 2,2-dimethyl succinate (DMS) buffer for biofilm development at 1% and 0.5% glucose concentrations with the reactor set at 1 rpm. The DMS buffer has been previously used for the optimization of ligninase production (27). Choice and use of buffer is of critical importance for economic considerations for larger scale operations.

DISK ROTATIONAL SPEED

Development of biofilm at 1 rpm invariably resulted in bridging between at least two of the discs, whereas this never occurred at 6.5 rpm. In addition, it appeared that the films at 6.5 rpm were more evenly distributed with an overall smoother surface. No difference in treatment activity was observed although dissolved oxygen concentrations at 6.5 rpm were generally double those at 1 rpm (Table 2). The influence of disk rotational rate maybe more pronounced for larger scale operations but the effects may be difficult to translate from bench scale.

TABLE 2. REACTOR PERFORMANCE TESTING

CONDITIONS		TOTAL AVERAGE REMOVAL(%)	
		UV WAVELENGTH (280 nM)	COLOR UNITS
% GLUCOSE	RPM		
1.0	1	28	71
		28	70
		17	49
1.0	6.5	25	66
0.5	1	22	46
		29	63
0.5	6.5	24	56
		30	59

KRAFT PULP MILL EFFLUENT VARIABILITY

Differences in sampling lots of the Kraft pulp mill effluent and changes in the lot during the time of storage may explain the variability of treatment results. For a total of five lots of effluent treated by our system, there were distinct changes in treatability. The sample lots of the effluent can differ significantly. Their composition depends on daily mill processes and feedstocks. Pulp mill effluent for softwood is typically dark in color, whereas the hardwood wastewater is less concentrated. No trend can be observed to identify the time interval for greatest treatment activity. Maximum treatment effects were observed for both early and late periods in the lifetime of the biofilms. An apparent toxicity developed within the effluent lots over time, normally encountered within 2 months after collection of the effluent supply. At this stage, fungal treatment became less effective and ultimately the fungus would not grow in the presence of that effluent lot. Toxins showing activity towards fungi have been previously noted in these effluents (24). Bacterial contamination is a possibility and is also suspected. Continuing investigation of this problem is required for full assessment of the bench scale treatment data.

AREAS OF CONTINUING INVESTIGATION

- The kinetic effects of oxygen and glucose concentrations on treatment.
- Influence of substrate for treatment on optimal conditions.
- Effluent variability and its control.
- Application to treatment of chlorinated phenols and polyaromatic hydrocarbons.
- Economic evaluation of operational factors.

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EVALUATION OF EPA SOIL WASHING TECHNOLOGY FOR REMEDIATION AT UST SITES

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ABSTRACT

The U.S. Environmental Protection Agency through its Risk Reduction Engineering Laboratory's Release Control Branch has undertaken research and development efforts to address the problem of leaking underground storage tanks (USTs). Under this effort, EPA is currently evaluating soil washing technology for cleaning up soil contaminated by the release of petroleum products from leaking underground storage tanks. Soil washing is a dynamic physical process which remediates contaminated soil via two mechanisms - particle separation and dissolution of the contaminants into the washwater. As a result of the washing process, a significant fraction of the contaminated soil is cleaned, and can be returned into the original excavation or used as cleaned "secondary" fill or aggregate material. Since the contaminants are more concentrated in the fine soil fractions, their separation and removal from the bulk soil increases the overall effectiveness of the process. Subsequent treatment will be required for the spent washwaters and the fine soil fractions.

The soil washing program evaluated the effectiveness of soil washing technology in removing petroleum products (unleaded gasoline, diesel/home heating fuel, and waste crankcase oil) from an EPA-developed Synthetic Soil Matrix (SSM) and from actual site soils. Operating parameters such as contact time, washwater volume, rinsewater volume, washwater temperature and effectiveness of additives were investigated. Further work was conducted to determine what, if any, effect additives have when added to washwater. The additives investigated were CitriKleen (a biodegradable degreasing agent) and an organic surfactant. Actual soils from UST sites in Ohio and New Jersey were washed using the optimum parameters derived for the SSM.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

* Prior to joining Chapman, Inc., in Freehold, NJ, Mr. Traver was the EPA Technical Project Monitor for this project.

INTRODUCTION

Based on the Hazardous and Solid Waste Amendments of 1984 and its Land Ban Regulations, EPA has discouraged the excavation and landfill disposal practices of the past for contaminated soils resulting from leaking underground storage tanks (USTs). EPA has encouraged the use of on-site treatment technologies, however, problems have plagued the development of on-site treatment technologies for the treatment of petroleum contaminated soils. Technical support is needed to develop effective long-term corrective actions at leaking UST sites, design cleanup program guidance, and help implement state programs.

The remedial options available for the treatment of contaminated soils from UST sites are broadly segregated into two main categories, namely those which remove the contaminants without excavation (in situ techniques) and those which require excavation of the soil and subsequent cleaning on-site. The former group of remedial options have not yet been demonstrated for high efficiency removal of contaminants from the subsurface. These techniques are plagued by the uncertainty of soil contamination levels in the subsurface after treatment. Soil excavation followed by extensive cleaning of the soil will ensure a more complete removal of contaminants over in situ techniques.

On-site soil washing of excavated soils is a viable alternative to in situ techniques and has been shown to be effective for the cleanup of hazardous waste contaminated soils (EPA, 1988). The goal of this effort is to determine the feasibility of soil washing for cleaning up petroleum contaminated soils.

Soil washing is a physical process in which excavated soils are contacted with a liquid medium, usually water. The two principle cleaning mechanisms include the dissolution of the contaminants into the extractive agent and/or the dispersion of the contaminants into the extraction phase in the form of particles (suspended or colloidal). The separation of the highly contaminated fine soil particles (silts, clay and colloidal) from the bulk of the soil matrix can result in volume reduction of the bulk soil. As a result, a significant fraction of the contaminated soil is cleaned and can be put back into the original excavation. Since the contaminants are more concentrated in the fine soil fractions, their removal from the bulk soil increases the overall effectiveness. Subsequent treatment will be required for the spent wash waters and the fine soil fractions.

Under Phase I of this research program, a synthetic soil matrix (SSM) containing a range of petroleum products at varying concentration levels was prepared and subjected to bench-scale performance evaluations of soil washing technology. Operating conditions derived from tests using SSM were used to evaluate soil washing technology on actual samples from leaking UST sites in Ohio and New Jersey.

Prior to preparing the quantities of SSM needed for the bench scale tests, several bench scale experiments were performed to develop a dose/response relationship between the quantity of petroleum product added to

the soil matrix and the analysis quantification. The petroleum products evaluated during this study include unleaded gasoline, diesel oil and waste crankcase oil. The SSM was then blended with a specific quantity of petroleum product to obtain a predetermined concentration level. Total petroleum hydrocarbon (TPH) analysis was performed to verify the concentration levels for diesel and waste oil, and benzene, toluene, ethylbenzene and xylenes (BTEX) analysis was performed to verify the concentration levels for gasoline.

The bench-scale washing experiments were designed to simulate the EPA-developed pilot-scale Mobile Soils Washing System (MSWS). Specifically, the bench-scale experiments were designed to simulate the drum-screen washer which separates the >2-mm soil fraction (coarse material) from the <2-mm soil fraction (fines) by use of a rotary drum screen. A high pressure water knife operates at the head of the system to break up soil lumps and strip the contaminants of the soil particles.

SYNTHETIC SOIL MATRIX CHARACTERIZATION

The basic formula for the SSM was determined by others from an extensive review of Superfund sites and a review of the composition of eastern U.S. soils (Traver, 1989 and PEI Assoc., 1988). The SSM was a mixture of clay, silt, sand, top soil and gravel, prepared by others in two 15,000-pound batches.

A review of the existing soil characteristics was made and additional tests were conducted to further delineate the physical and chemical properties of the SSM. The tests included particle size distribution, moisture retention, Atterberg limits, cation exchange capacity, base saturation, organic matter, chemical constituents and mineralogy. Quantification and assessment of these specific properties will assist the technical community to understand the differences that may be observed between the performance of soil washing technology on the SSM and on actual UST site soils. The results of the characterization tests are presented in Tables 1-5 and Figures 1 and 2.

The test results indicated that the SSM is composed of 60 percent sand, 19 percent silt and 21 percent clay as determined by particle size distribution analysis (Table 1 and Figure 1). Based on this composition the SSM would be classified (USDA) as having a sandy clay loam texture.

The moisture content of the SSM ranged from 33.1 percent at saturation (0 bar) to 8.7 percent at the permanent wilting point (15 bars). The moisture content at field capacity (0.1 bar) was 21.0 percent. The moisture-retention curve (Figure 2) developed from the moisture content data was indicative of a finer textured soil. The moisture content data can be used to evaluate moisture and chemical characteristics of the SSM. For example, the amount of soil water that can be extracted from the SSM under typical environmental conditions (0 to 15 bars) will be 24.4 percent. The remaining soil water is considered as "unavailable", which can only be removed by artificially induced vacuums or pressures.

DOSE/RESPONSE TEST

The purpose of the dose/response test was to determine the appropriate amounts of gasoline or diesel fuel which should be added to the SSM to obtain the desired concentration of selected constituents or parameters (e.g., BTEX or TPH). Various mixtures of SSM and gasoline or diesel were prepared and the soil analyzed for benzene, toluene, ethylbenzene and xylenes (BTEX) and total petroleum hydrocarbons (TPH).

The procedure used was to place known amounts of SSM, water, and either gasoline or diesel into wide mouth glass jars. The contents were mixed by hand for five minutes, and then the contents were submitted to a laboratory for analysis of TPH and BTEX.

The results of the dose/response tests are shown in Table 6. The lab tests indicate that the soils reach a level of liquid saturation at about 23% liquid (both water and gas or diesel). The tests were conducted such that the soils were all prepared to a 20% water level. However, this limited the amount of gas or diesel which could be mixed into the soil mixture. At 20% water, the highest achievable BTEX concentration was about 3000 mg/kg. For diesel, at water content of 20%, the highest TPH concentration was 60,000 mg/kg.

The dose/response curves are plotted in Figures 3 and 4. A linear regression of the data yielded the following relationships for dose/responses:

Gasoline:

G = gasoline concentration, mg/kg

B = BTEX concentration (sum of benzene, toluene, ethylbenzene, and xylenes), mg/kg

$$G = 13.33(B) - 375 \quad (1)$$

The correlation coefficient r , for this equation is 0.998.

Diesel:

D = diesel fuel concentration, mg/kg

T = TPH concentration, mg/kg

$$D = 0.675(T) + 6268 \quad (2)$$

The correlation coefficient r , for this equation is 0.995.

An additional experiment was conducted to determine if a higher level of BTEX could be achieved if a lower moisture content was used. In this experiment, a sample of soil was moistened to a 10% water content and then saturated with gasoline. The results, shown in Table 6 as "Jar 9", indicated that the BTEX content was increased to 4670 mg/kg.

Equations 1 and 2 can be used to determine the amount of diesel or gasoline to add to the SSM to reach the desired concentrations. Based on these calculations, estimates were made to determine the amount of gasoline and diesel fuel to add to the SSM to obtain the desired concentrations of BTEX and TPH for the bench scale experiments. The SSM blends were prepared in the EPA SSM Blending Facility in Edison, NJ in 50-lb batches for use in the bench scale soil washing experiments.

BENCH SCALE SOIL WASHING TESTS

The experiments involved washing the SSM spiked with gasoline, diesel fuel, or waste crankcase oil under several operating conditions to obtain the sensitivity of various parameters affecting soil washing efficiency.

The experiments were conducted by contacting approximately 1400 g of soil with varying amounts of washwater. The contact time was varied as was the rinsewater volume. The washing of the soils was conducted by shaking the soil and washwater in a 2-gallon jar in a shaker table operating with a stroke and frequency of 1.6 inches and 4 Hz respectively. The rinsing of the soils was performed in a Gilson Wet-Vac Model WV-1 which both rinsed the soils as well as separated the particles into three fractions using No. 10, No. 60 and No. 140 sieve trays. The process of the washing and rinsing yielded five distinct fractions - the soils on the three sieve trays, a washwater, and a rinsewater. All fractions were measured for mass (or volume) as well as contaminant concentration. A measure of total BTEX (benzene, toluene, ethylbenzene and o-, m-, and p-xylenes) was used on gasoline spiked soils, and total petroleum hydrocarbons (TPH) was used on diesel spiked soils.

Preliminary screening tests were conducted on soils spiked with diesel and gasoline to determine the optimum conditions for contact time, washwater volume, rinsewater volume and washwater temperature. The parameters tested are listed in Table 7 along with an assessment of how the parameter affected removal of TPH or BTEX from the soil and on the particle separation during the washing process. As shown in this table, most parameters had minimal effect on the removals and particle separation for the ranges tested. Increased contact time did somewhat improve the contaminant removal and particle separation. The addition of CitriKleen did not improve contaminant removal, and in fact actually decreased the removals. Increased temperature did not improve removals for soils washed with plain water, but did improve the removals somewhat for washwaters containing CitriKleen or surfactant. Typical results obtained for these experiments are shown in Table 8.

The results of the experiments indicate that the optimal washing conditions for SSM spiked with diesel or gasoline are: 20-to 30-minute contact time, 1:1 soil to washwater mass ratio, 3:1 rinsewater to washwater volume ratio, and ambient temperature for the washwater. These conditions resulted in a 90+% removal of TPH and BTEX in the No. 10 and No. 60 sieve fractions. It should be noted that these conditions represent the most cost-effective operating conditions for bench scale treatment of SSM using soil washing technology. Operating conditions for each site soil may vary and should be determined on a case by case basis.

Experiments were then conducted on site soils from four UST sites located in Ohio and New Jersey. The results, shown in Table 9, indicate that the removals in the 10 and 60 sieve fraction were significantly lower than the removals achieved for SSM. The site soils had a significantly different particle size distribution than the SSM, as shown in Table 10. The bench scale soil washing apparatus was able to recover only 55% of the SSM mass after washing, and 45% was washed off into the washwater and rinsewater. Since the site soils contained lower amounts of fines (7 to 43% by weight for the four sites tested), greater amounts of soil were recovered from the washing process, resulting in lower suspended solids in the washwaters, as shown in Table 11.

SUMMARY AND CONCLUSIONS

The soil washing experiments involved washing the SSM spiked with gasoline, diesel fuel, or waste crankcase oil under several operating conditions to obtain sensitivity analyses on various parameters affecting soil washing efficiency including: contact time with washwater, washwater volume, washwater temperature, and chemical additives to the washwater such as a surfactant and a degreasing agent (CitriKleen). The SSM experiments yielded highly reproducible results. Since the soils were prepared in the SSM blending facility, the soil characteristics and contaminant content were homogeneous throughout the matrix. Experiments were also conducted using actual site soils, but due to the heterogeneity of these soils, the reproducibility of these experiments was much lower than for the SSM.

The results of the optimization tests using SSM indicated that removals greater than 90% of petroleum products could be achieved for the SSM. However, as washing conditions were varied, no significant change in the removals could be detected for most parameters tested. The contact time in the wash cycle affected the percent removal possibly due to improved mechanical separation of the fines from the larger particles with more shaking time in the wash step. Increased washwater and rinsewater volumes did not significantly improve contaminant removal. The use of additives such as CitriKleen and surfactant did not improve removal of contaminants. Increased amounts of CitriKleen in the washwater caused decreased removals of contaminants which may be attributed to enhanced adsorption of contaminants to the soil due to the presence of CitriKleen adsorbed onto the matrix. Experiments using surfactant resulted in considerable foaming which would lead to operational problems in pilot or full scale operation.

The experiments using actual site soils resulted in lower removals of contaminants than for the SSM experiments using the same washing conditions. The washwaters for the actual site soils also contained much lower suspended solids than the SSM washwaters. These results indicate that the primary mechanism for contaminant removal for the SSM was particle separation. Since this mechanism alone was able to account for a high percentage of contaminant removal, the experiments showed no significant improvement when conditions were varied. The only parameters which seemed to improve removals were those which would improve the particle separation in the soil matrix.

Although the SSM experiments achieved high removals, only 55% of the washed soil mass was recovered, and a washwater containing over 20% solids was produced. The washwaters from the actual site soils experiments had lower suspended solids, but also resulted in lower contaminant removals from the soil matrix. Therefore, enhancement of the solubilization mechanism would be required to effectively remove contaminants from soils containing a small fraction of fine materials. The resultant washwaters would also contain lower suspended solids. Future work to evaluate the enhancement of the solubilization mechanism in soil washing is recommended.

REFERENCES

- EPA Office of Solid Waste and Emergency Response, Assessment of International Technologies for Superfund Applications, EPA/540/2-88/003, (1988).
- PEI Associates, Inc. CERCLA BDAT SARM Preparation and Results of Physical Soil Washing Experiments, Cincinnati, OH (1988).
- R.P. Traver, Development and Use of EPA's Synthetic Soil Matrix (SSM/SARM). U.S. EPA Releases Control Branch, Risk Reduction Engineering Laboratory, Edison, NJ (1989).

TABLE 1. USEPA SYNTHETIC SOIL MATRIX PARTICLE SIZE DISTRIBUTION (USDA)

SOIL FRACTION	USDA(%)	USCS(%)
Gravel	--	--
Sand (Total)	60.0	58
Very Coarse	16.0	
Coarse	8.8	
Medium	11.7	
Fine	23.5	
Silt	19.0	15.2
Clay	21.0	26.8

TABLE 2. USEPA SYNTHETIC SOIL MATRIX CHEMICAL CHARACTERISTICS

PARAMETER	UNITS	VALUE
Organic Matter	%	1.3
pH	--	8
Cation Exchange Capacity (CEC)	meq/100g	21.7
Base Saturation	%	99%
Ca		86.2
Mg		12.4
K		1.3
H		0
Available Phosphorous	ppm	
Weak Bray		20
NaHCO ₃		31
Potassium	ppm	112
Magnesium	ppm	324
Calcium	ppm	3740

TABLE 3. USEPA SYNTHETIC SOIL MATRIX X-RAY FLUORESCENCE ANALYSIS - MAJOR CONSTITUENTS (ppm)

PARAMETER	SAMPLE	DUPLICATE	COMMON* RANGE
Silica Dioxide (SiO_2)	37.9	39.6	49-75
Calcium Oxide (CaO)	21.5	22.3	1-70
Aluminum Oxide (Al_2O_3)	7.85	8.1	2-57
Magnesium Oxide (MgO)	4.03	4.25	0.1-1.0
Magnetite (Fe_2O_3)	3.64	3.78	1-79
Potassium Monoxide (K_2O)	1.38	1.44	0-3.6
Titanium Dioxide (TiO_2)	0.44	0.45	0.2-1.7
Sodium Monoxide (Na_2O)	0.34	0.37	0-1.0
Phosphoric Acid (P_2O_5)	0.31	0.33	0-1.2
Manganese Oxide (MnO)	0.15	0.15	0-4.0
Barium Oxide (BaO)	0.03	0.04	0-0.3
Chlorine (Cl)	0.02	0.02	0-0.0009
Sulfur (S)	<0.05	<0.05	0-1.0

* Source: Based on Lindsay (1979)

TABLE 4. USEPA SYNTHETIC SOIL MATRIX X-RAY FLUORESCENCE ANALYSIS - TRACE ELEMENTS (ppm)

PARAMETER	SAMPLE	DUPLICATE	COMMON* RANGE
Strontium (Sr)	369	390	50 - 1000
Zirconium (Zr)	349	370	60 - 2000
Chromium (Cr)	131	135	1 - 1000
Vanadium (V)	57	58	20 - 500
Zinc (Zn)	46	46	10 - 300
Rubidium (Rb)	41	46	50 - 500
Yttrium (Y)	43	40	25 - 250
Wolfram (W)	28	32	--
Lead (Pb)	22	25	2 - 200
Nickel (Ni)	14	15	5 - 500
Copper (Cu)	12	14	2 - 100
Tin (Sn)	<50	<50	2 - 200
Arsenic (As)	<20	<20	1 - 50
Thallium (Tl)	<10	12	--
Molybdenum (Mo)	<10	<10	0.2 - 5
Uranium (U)	<10	<10	--
Niobium (Nb)	<10	<10	--
Cobalt (Co)	<10	<10	1 - 40

* Source: Based on Lindsay (1979)

TABLE 5. USEPA SYNTHETIC SOIL MATRIX - X-RAY DIFFRACTION CLAY MINERALOGY

MINERAL	% SAMPLE
Quartz	27
Calcite	27
Dolomite	18
Plagioclase feldspar	8
K-feldspar	8
Smectite/vermiculite	5*
Kaolinite	<5*
Mica/illite	--
Chlorite	--
Polygorskite/attapulgite	--
"Unidentified"	<5

* Estimated concentration. Quantification not possible due to low concentration of mineral.

TABLE 6. SOIL WASHING DOSAGE/RESPONSE TESTS

Jar No.	Gasoline Concentration (mg/kg)	% Water	BTEX Concentration (mg/kg)	TPH Concentration (mg/kg)	Dose/ Response Ratio
1	6,100	21	400	NT	15
2	30,200	20	2,200	NT	14
3	58,300	16	4,420	390	13
4	14,600	20	1,280	NT	11
9	86,000	10	4,670	NT	18

Jar No.	Diesel Concentration (mg/kg)	% Water	BTEX Concentration (mg/kg)	TPH Concentration (mg/kg)	Dose/ Response Ratio
5	6,200	20	NT	1,950	3
6	16,000	20	NT	13,300	1
7	31,000	20	NT	33,500	1
8	47,700	20	98.3	63,500	1

NOTES:

NT - Not Tested

TABLE 7. EFFECT OF TESTED PARAMETERS ON SOIL WASHING EFFICIENCY OF SSM

VARIED PARAMETER	RANGE	EFFECT ON CONTAMINANT REMOVAL	EFFECT ON PARTICLE SEPARATION
Contact Time	10-30 min	0/+	+
Soaking Time	15-30 min	0	0
Soil/Washwater Ratio	0.5-2	+	0
Rinsewater/Washwater Ratio	3-10	0	0/+
CitriKleen	0-0.7%	-	0
Washwater Temperature	55-180°F	0	0/+
0.13% CitriKleen/Temp.	55-180°F	+	0
0.5% Surfactant/Temp.	75-120°F	0/+	+

NOTES:

- + = improvement
- 0 = no effect
- = negative effect

TABLE 8. REMOVAL EFFICIENCIES FOR SSM SOIL WASHING EXPERIMENTS

SOIL CONTAMINANT	INITIAL CONCENTRATION	WASHING SOLUTION	PERCENT REMOVAL		
			#10 SIEVE	#60 SIEVE	#140 SIEVE
Gasoline	2,100 mg/kg BTEX	77°F Water	99	99	99
Gasoline	2,100 mg/kg BTEX	77°F 0.5% Surfactant	93	98	94
Diesel	18,000 mg/kg TPH	77°F Water	99	98	98
Diesel	18,000 mg/kg TPH	77°F 0.67% CitriKleen	99	97	--
Diesel	18,000 mg/kg TPH	178°F Water	99	99	99
Waste Oil	1,100 mg/kg TPH	77°F Water	97	98	85
Waste Oil	9,300 mg/kg TPH	77°F Water	96	98	92

NOTE: All above experiments conducted with the following parameters held constant: 30 minute contact time, 1:1 soil/washwater ratio, 3:1 rinsewater/washwater ratio.

TABLE 9. ACTUAL SITE SOILS REMOVALS

SITE LOCATION	PERCENT REMOVAL		
	#10 SIEVE	#60 SIEVE	#140 SIEVE
Grove City, OH	10	49	49
(gasoline)	67	50	--
Mahwah, NJ	16	80	14
(gasoline)	77	89	--
Princeton, NJ	82	72	83
(home heating fuel)	86	0	--
Holmdel, NJ	91	54	49
(kerosine)	97	91	70

Notes:

- (1) Percent removal calculated based on initial bulk soil concentration using the following relationship.

$$\text{Percent Removal for Sieve Fraction} = \frac{\text{Bulk soil conc.} - \frac{\text{washed sieve fraction conc.}}{\text{Bulk soil conc.}} \times 100$$

- (2) All experiments performed in duplicate.

TABLE 10. PARTICLE SIZE DISTRIBUTION OF SOILS

SITE LOCATION	PERCENT IN EACH FRACTION			
	#10 SIEVE	#60 SIEVE	#140 SIEVE	WASHWATER AND PINSEWATER
SSM	13	31	11	45
Grove City, OH	30	50	4	16
Mahwah, NJ	26	43	21	10
Princeton, NJ	23	12	8	43
Holmdel, NJ	14	67	12	7

TABLE 11. SUSPENDED SOLIDS LEVELS IN WASHWATERS AND RINSEWATERS

SOIL	SUSPENDED SOLIDS (mg/L)	
	WASHWATER	RINSEWATER
SSM	228,000	6,070
Grove City, OH	33,000	3,100
Mahwah, NJ	40,600	3,060
Princeton, NJ	110,000	6,180
Holmdel, NJ	40,600	6,820

NOTE: Results are for experiments conducted with 30 minute contact time, 1:1 soil to washwater ratio, 3:1 rinsewater to washwater ratio.

Figure 1 U.S. EPA Synthetic Soil Matrix
Particle Size Distribution Curve

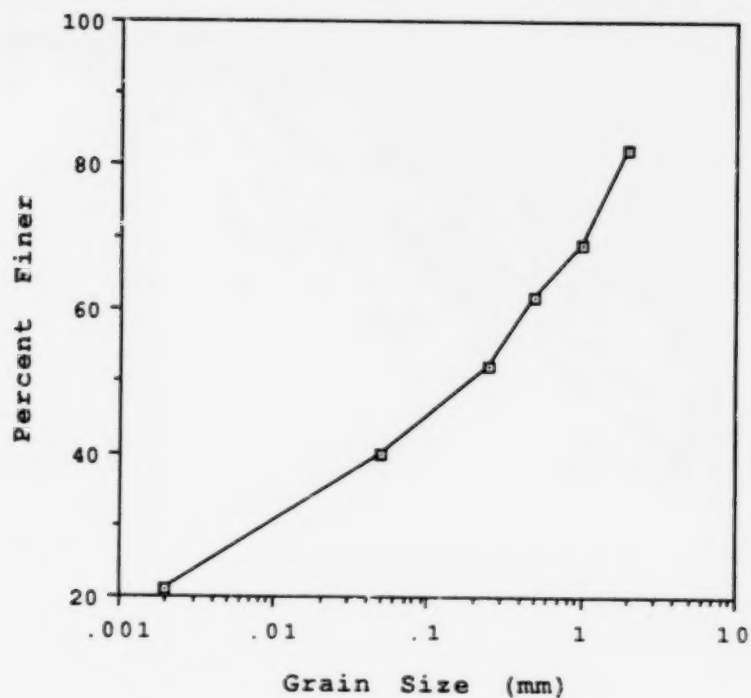


Figure 2 U.S. EPA Synthetic Soil Matrix
Moisture Retention Curve

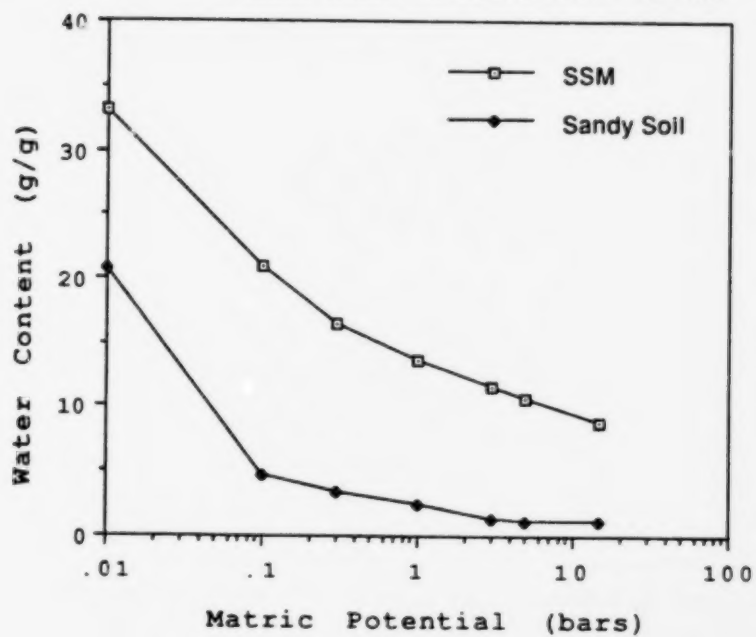


Figure 3 Dose/Response Curve for Gasoline

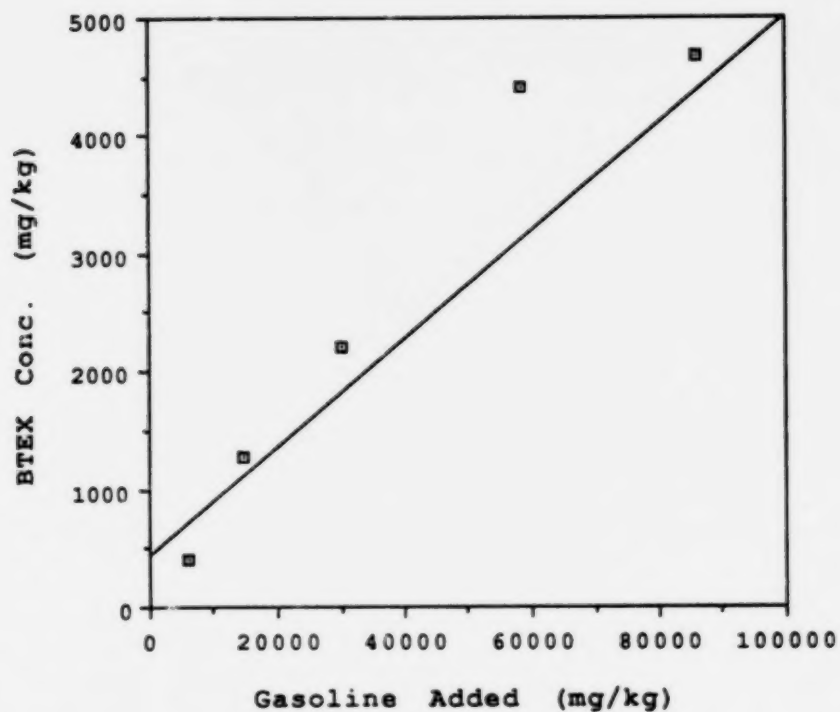
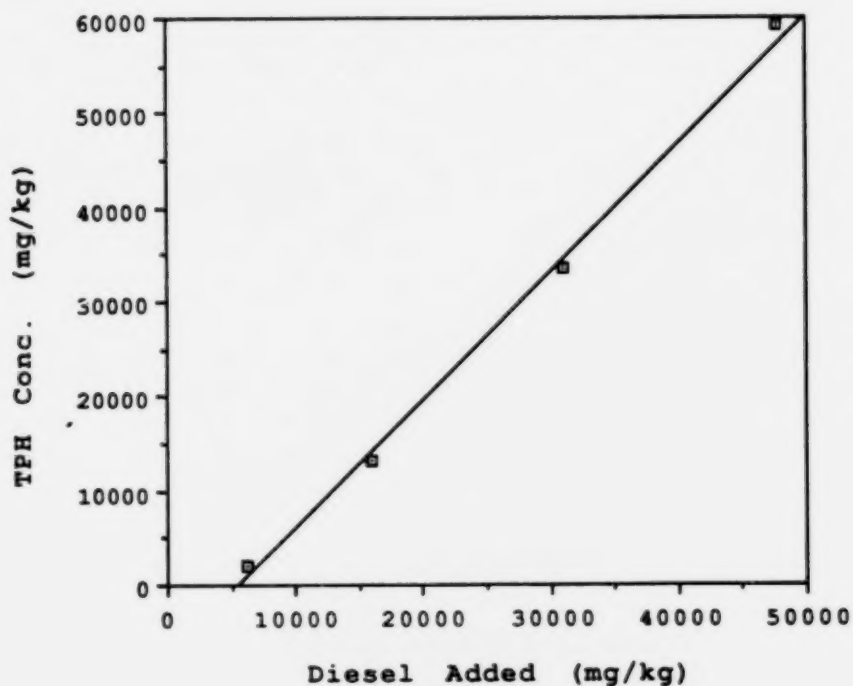


Figure 4 Dose/Response Curve for Diesel Fuel



Vacuum-Assisted Steam Stripping to Remove Pollutants from Contaminated Soil A Laboratory Study

by

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ABSTRACT

A project is underway to evaluate the vacuum-assisted steam stripping procedure for removal of organic contaminants from soils. The first two years of the study were devoted to determination of basic parameters such as steam permeability and pollutant removal efficiency. A wide variety of soils were used and the "pollutants" were kerosene and a series of simple organic chemicals of widely varying boiling point and polarity. These results were reported in the previous two Symposiums. The vacuum-assisted steam stripping technique appears to have significant potential for pollutant removal from soils. A unique composite geosynthetic cap was developed for the field vacuum-assisted steam stripping application.

The present paper concentrates on the ability of steam stripping to remove high boiling point materials. Dodecane (b.p. = 216°C) was used with a 50% sand - 50% silt soil mixture. Steam pressures of 3, 5, 10 and 11.5 psi were utilized. The original level of dodecane (5% by weight) was reduced by two and one half orders of magnitude in 6 hours of steam stripping at 11.5 psi. This is considerably better than we reported at last year's Conference, at lower steam pressures.

Also presented are data comparing steam stripping, vacuum stripping, air stripping and heat stripping of kerosene from sand and a 50% sand - 50% silt soil mixture under a variety of temperatures. It appears from the laboratory testing that steam stripping is the most thorough soil decontamination method.

INTRODUCTION AND OVERVIEW

With contaminated soils at Superfund (and other) sites, it is important that the chemicals be prevented from reaching the groundwater. Fortunately, in many locations the partially saturated or vadose zone exists and acts as temporary containment retarding the downward movement of the pollutant. The remediation options are:

- Excavation and off-site disposal.
- Excavation and on-site treatment.
- Insitu treatment (via a number of possible methods, e.g., biological, physical or chemical).

A number of these techniques (and others) have been reviewed in recent articles (1,2). These in-situ techniques have been discussed by the authors (3).

The present study falls in the in-situ treatment category wherein the authors propose to have pipes inject steam into the soil beneath the contaminated zone. Steam stripping of the chemical occurs and when aided by a vacuum at the ground surface brings the contaminants to a collection point where they can be properly treated. A unique aspect of the study is the development of a geosynthetic cap assembly consisting of a high transmissivity geotextile and a flexible membrane liner (geomembrane). The vacuum is applied to the underside of this liner and the contaminated gas and/or liquid moves beneath the liner in the geotextile to the outlet ports. A schematic diagram of a proposed system is given in Figure 1 for reference purposes.

There have been a few steam stripping soil decontamination studies reported in the literature (4,5,6,7). These works were field-oriented, sites-of-opportunity projects with no attempt to look at the general problem of the feasibility of steam stripping a wide variety of chemicals from a wide variety of soils.

The present work continues a long term study to determine the ability of vacuum-assisted, steam stripping to decontaminate general organic chemical species from a variety of soil types.

PREVIOUS WORK ON THIS PROJECT

The work performed in the first phase of the project has been reported in detail elsewhere (3,8,9,10). Only a brief review of the results of this work will be given here. Among the tasks undertaken, in a wide variety of soils were:

- Observations were made of the transient steam front movements in two dimensional flow.
- The steam permeabilities were determined in conventional one-dimensional flow.
- The efficiency of steam stripping kerosene and a number of individual organic chemicals from soils was determined. The chemicals included dodecane, decane, octane, octanol and butanol. The analytical methods included either volume separation of the outflow material (for kerosene) or gas chromatography (GC) of extractions from the soil (for the pure compounds).
- A steady state analytical model was developed where steam flowed upward to the collection cap from pipes embedded in the soil. Use of this model allowed calculation of the decontamination time for a given kerosene spill*.
- A small scale model of the geosynthetic cap was fabricated and used to determine its feasibility as a cover assembly during steam stripping. A schematic diagram of the experimental setup is shown in Figure 2.

The results from the above topics indicated that the vacuum-assisted steam stripping technique showed significant promise as a soil decontamination method for a wide range of soil types and chemicals.

*Certain objections have been raised concerning the model and its use. Currently work is underway in the development of an alternate model.

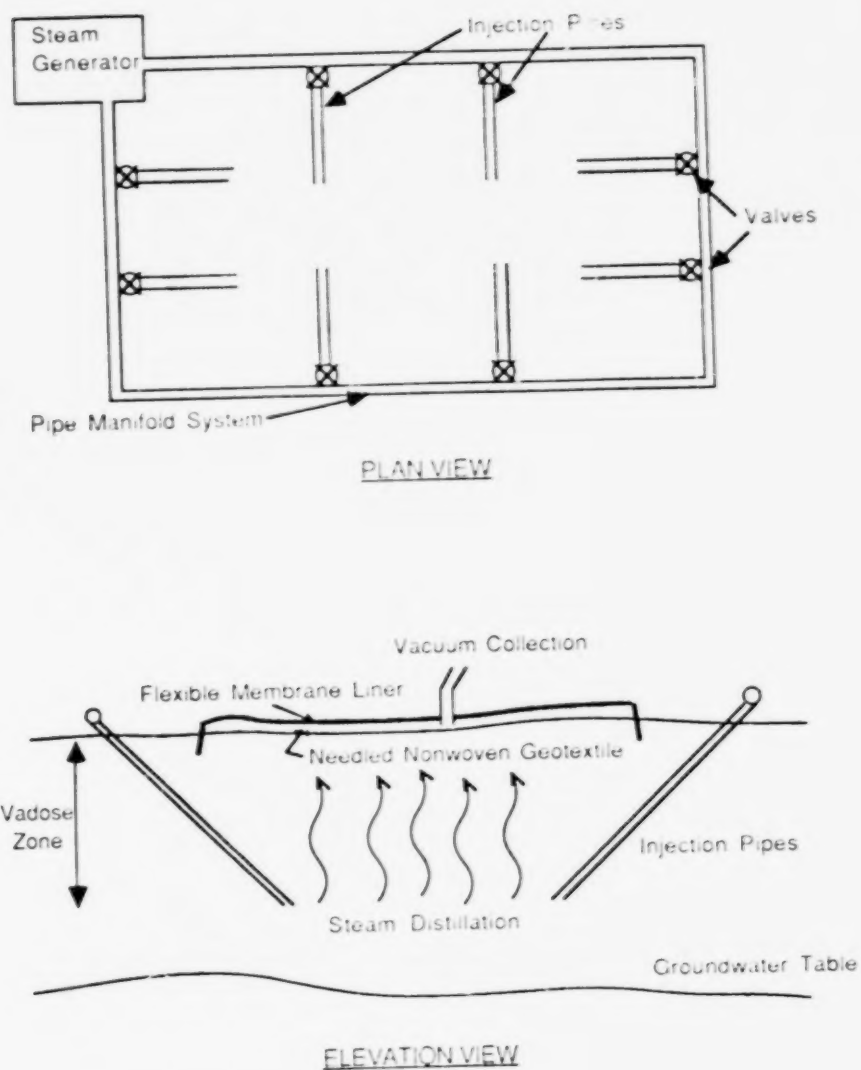


Figure 1 - Proposed In-Situ Vacuum-Assisted Steam Stripping Field Apparatus

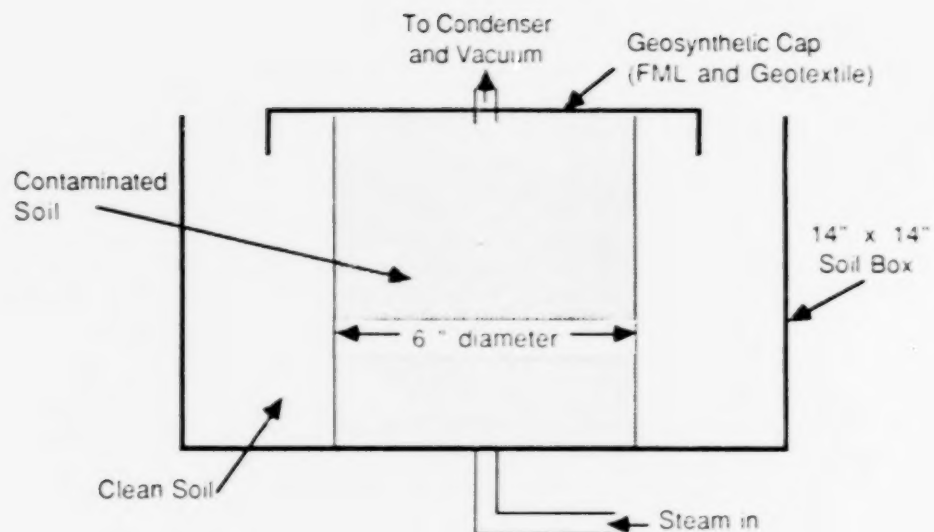


Figure 2 - Pilot Scale Experiment for Vacuum-Assisted Steam Stripping Using the Geosynthetic Cap

As a result of the previous work (including the literature search), certain aspects of the problem needed to be addressed in further work. These include:

- Determining the limits of confidence in the soil extraction/gas chromatography analytical procedure.
- Determining the effect of steam pressure and temperature on the steam stripping capability.
- Comparison of the efficiency of steam stripping versus the other common in-situ techniques, i.e., air stripping, vacuum extraction and heat alone.
- Determining if the rate of chemical removal changes subsequent to a long delay period following partial chemical removal by steam stripping (or other decontamination methods).

PRESENT WORK

Accuracy of Chemical Analysis

As discussed at the last Symposium, there was concern as to the accuracy of the soil extraction/GC method used in the chemical analysis. Therefore work was undertaken in this regard. As a first step, the GC extraction fluid, ethyl ether was "doped" to given values of three common organic compounds. The compounds were dodecane, toluene and o-xylene. The levels of doping were 5 μ l, 20 μ l and 100 μ l in 50 ml of the ethyl ether. The samples were given to our Chemistry Department co-workers, the amounts of the dopants being unknown to them. Standard reduction in volume techniques were used on the extracts to concentrate the chemical, and then GC analysis was performed. With very few exceptions (for 24 of the 27 samples provided) the GC analysis gave values which were within 20% of the actual doped levels.

As a second step (and more difficult assessment) dodecane was introduced into a 50% sand/50% silt soil sample. The levels of doping were 10, 40 and 100 μ l and the soil weight was 50 grams. These correspond to 150, 600 and 1500 ppm (by weight) of dodecane in the soil. The dodecane was mixed as thoroughly as possible into the soil, allowed to sit for 20 hours and then extracted with the ethyl ether. Three-fold extraction was used with vigorous hand-mixing during each extraction. The extracted fluid was reduced in volume and then GC analysis was performed. The results are shown in Figure 3. It is seen that poor agreement exists between the GC results and the doped amounts at the lower levels. This could be due to certain causes:

- a certain amount of dodecane becomes attached to the finer soil particles and thus resists extraction
- large percentage loss of these very small volumes of dodecane during extraction (evaporation, attachment to container walls, stirring rods, etc.). It was however attempted to minimize all these effects

The results of Figure 3 may not be completely pertinent to the general question of soil analysis accuracy (due to some of the problems raised above), but they should certainly be folded into any final conclusions. It is interesting to note that an average of 35 μ l is missing in both the 100 μ l and 40 μ l doped samples. This may be the amount that is attached to the fine-grain silt particles. There has been work done by soil chemists in "spiking" soils with various priority

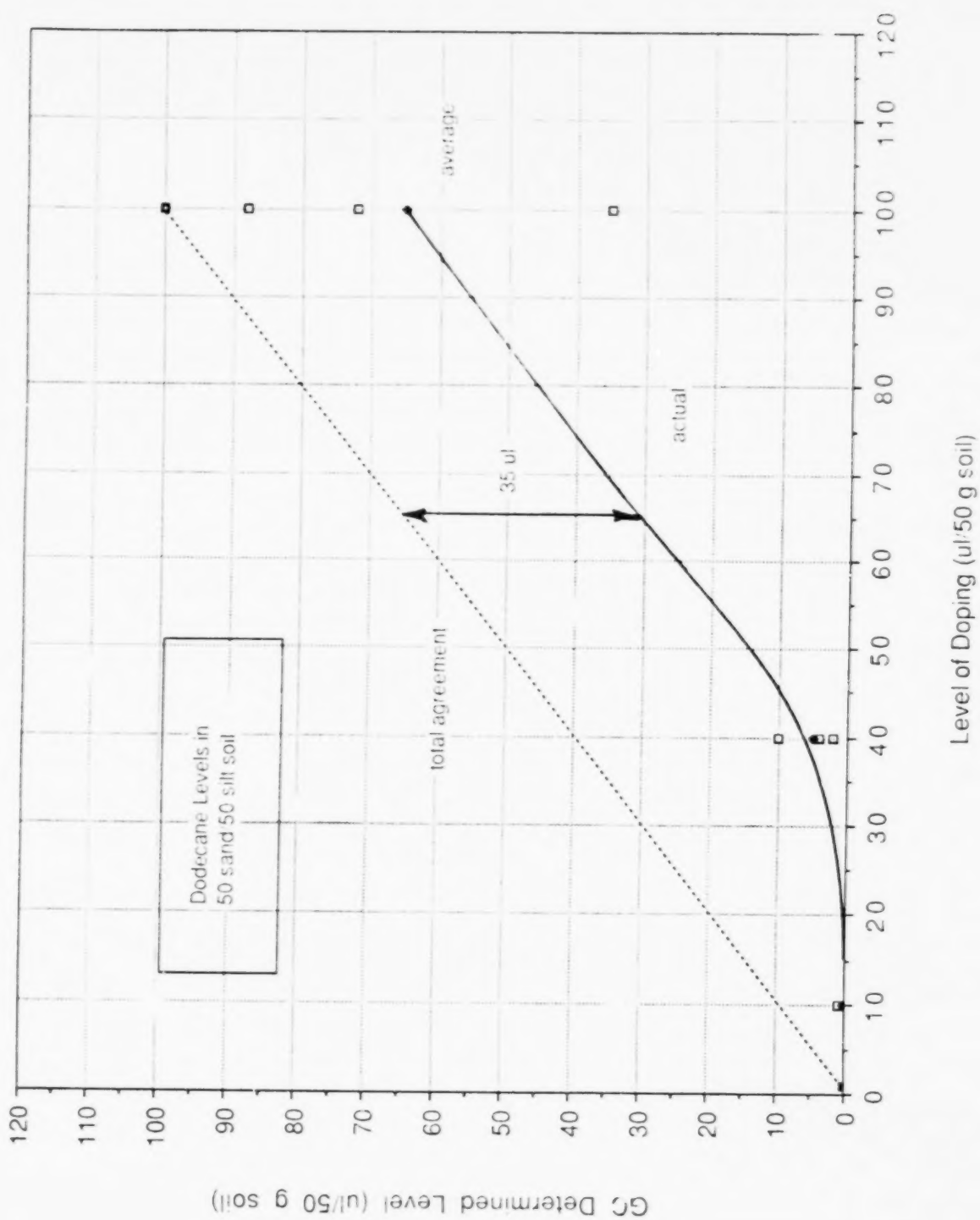


Figure 3 - GC Determined Level of Doping Versus True Level

pollutants to determine the recovery rate on subsequent extraction for GC analysis (11). Recovery rates for the various compounds are variable (some few being non-recoverable), but many are in the region of 70-80%. Unfortunately, no analysis of the soil (grain size distribution, etc.) is given (11).

Effect of Steam Pressure (and Temperature) on Steam Stripping Efficiency

In the previously reported work (3,8,9,10) the steam pressure available was limited to the house steam and was nominally about 5 psi gauge (with some variations and even inadvertent cessations.) A steam generator was therefore purchased allowing well-controlled steam pressures from 3 to 30 psi to be available. (A pressure of 11.5 psi was the highest that could be achieved because of the large volume of steam which was flowing.) Figure 4 is a schematic diagram of the vessel constructed to allow a determination of the effect of steam pressure (and hence also temperature) on the steam stripping ability of given chemicals from a soil sample. Steam passes through the outside dual-wall of the container in order to keep the walls hot and lessens excessive steam condensation.

Steam passes through the soil sample (6 inch diameter $\times$ 2 inches high) which is contained on the top by a porous plate which precludes the soil from being blown out of its position by the steam pressure. The soil temperature and steam pressures are monitored as per Figure 4. Dodecane (at 5 wgt %) was used as the chemical and the soil was a 50% sand/50% silt mixture.* The soil was analyzed for residual dodecane after various steam stripping scenarios. The results of this work are shown in Figure 5. Here is plotted the amount of dodecane remaining in the soil as a function of time at steam pressures of 3, 5, 10 and 11.5 psi. (The measured temperature of the soil was essentially independent of steam pressure and remained very near to 100°C).

It is seen in Figure 5 that while the initial removal rates seem to be relatively independent of steam pressure†, the higher steam pressures reduce the residual dodecane level much lower at the longer times. (We, of course, are assuming here that these relatively large differences are real, and are not grossly affected by the problems shown with the soil extraction/GC analysis method discussed earlier). The level of 150 ppm reached at 11.5 psi in 6 hours is considerably lower than the value of 1000 ppm reported in last year Proceedings (while using ~5 psi steam in a different cell).

Efficiency of Steam Stripping and Other Decontamination Methods

Figure 6 shows the efficiency of kerosene removal in both sand and the 50% sand/50% silt mixture, in the aforementioned small laboratory samples. The steam pressure used here was about 5 psi and the vacuum was 10 inches Hg for sand and 20 inches Hg for the 50/50 mixture. In the case of sand the kerosene is completely removed (as far as volumetric separation analysis tells) in a very short time. For the 50/50 mixture the volumetric separation analysis indicates that some 30% of the kerosene is remaining after 700 minutes of steam stripping. However the output fluid was colored indicating some kerosene content. Carbon Oxygen Demand (COD) analysis of the output fluid as a function of time (9) allowed a more reliable curve of kerosene removal to be ascertained. The results of this correction process is shown in Figure 7. (It should be emphasized that the COD correction procedure is not exact, but it gives a much clearer picture than that represented by the uncorrected curve.)

In order to compare steam stripping with other decontamination techniques, laboratory experiments were also performed with vacuum, air and heat stripping of kerosene from sand and

*The properties of this soil can be found in reference 3.

†The initial removal may simply be a physical "pushing out" of the chemical from the soil.

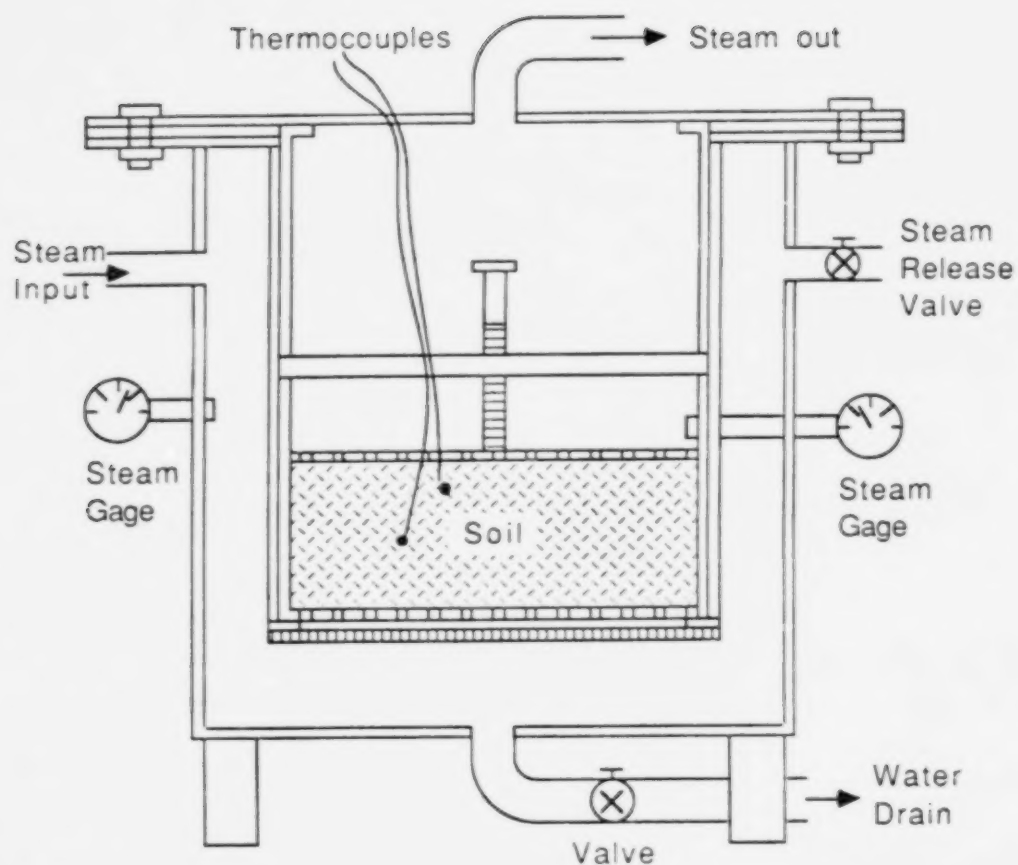


Figure 4 - Schematic Diagram of Device to Steam Strip Soil Sample at Various Pressures

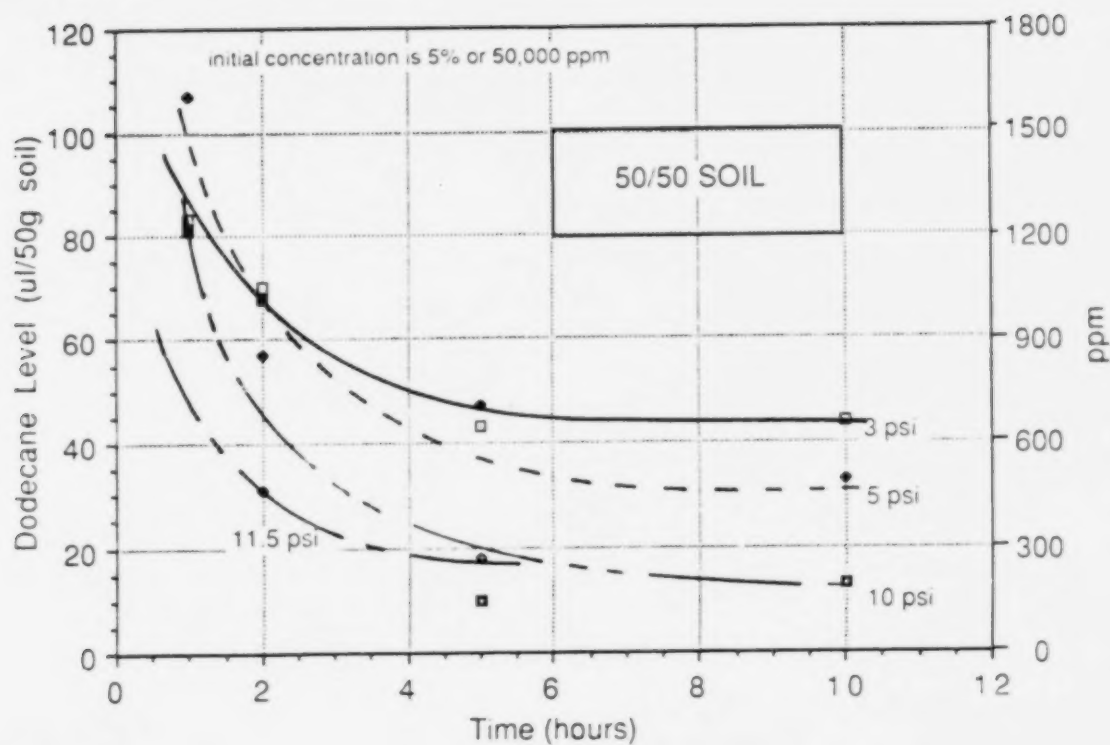


Figure 5(a) - Steam Stripping GC Results

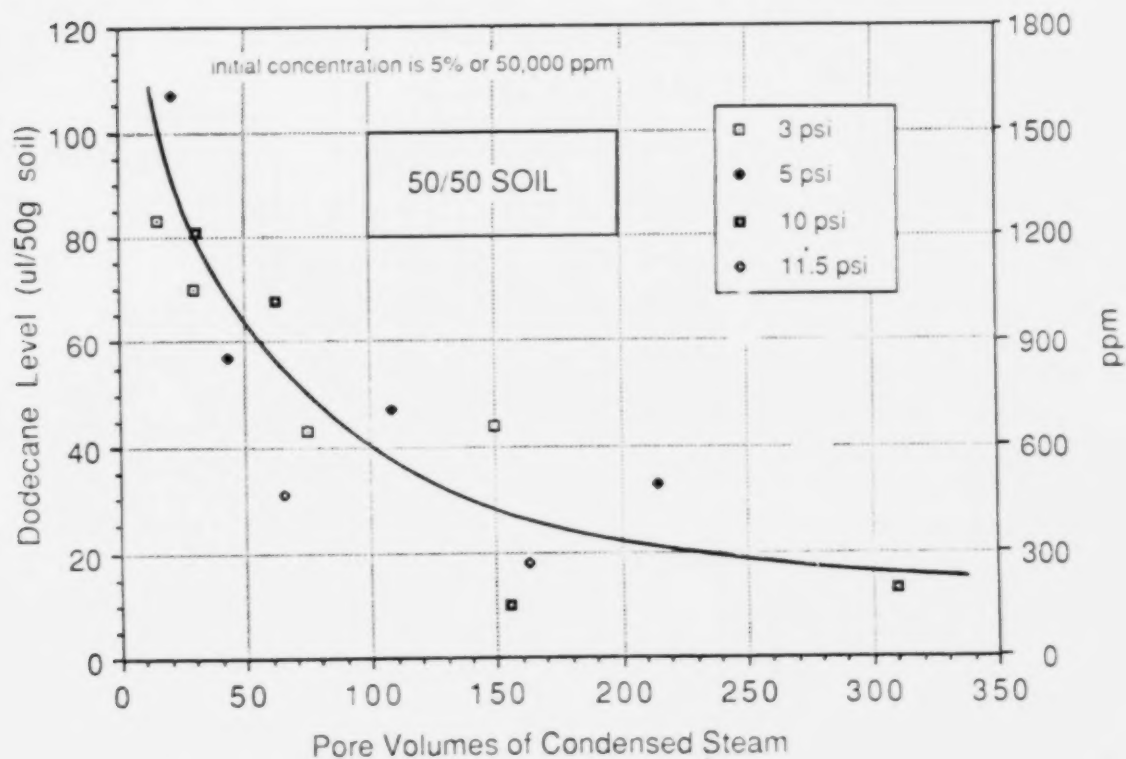


Figure 5(b) - Steam Stripping GC Results

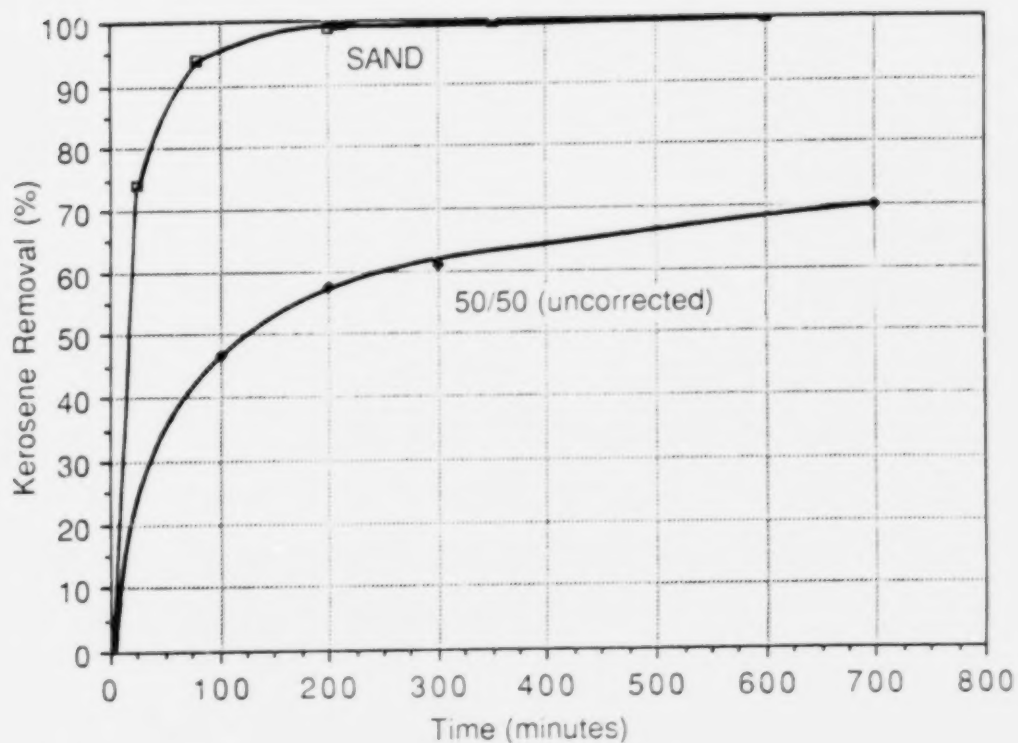


Figure 6 - Kerosene Removal via Steam Stripping

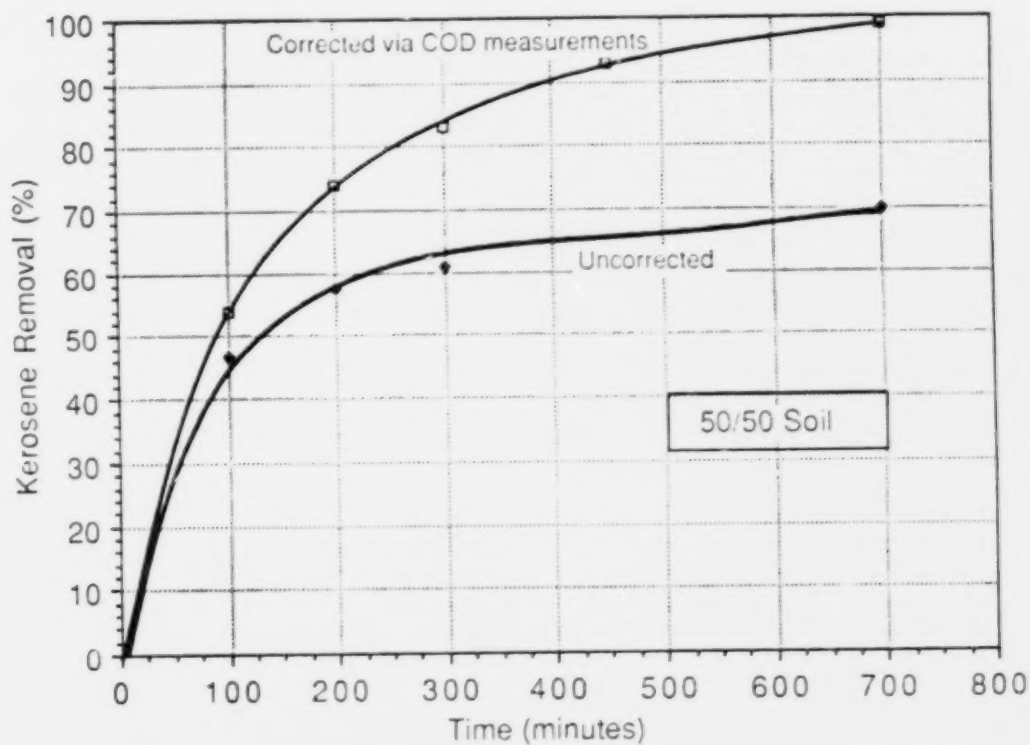


Figure 7 - Kerosene Removal via Steam Stripping (COD corrected)

the 50/50 soil. In these cases, the soil was dried and outgassed at 500°C for two hours to ensure stability. The soil sample was then placed in the small laboratory cells (2.5-inch diameter × 6-inches high) and "doped" to the given level of kerosene (about 20%). The cells were then placed in a furnace at a given temperature (see Figure 8) and either (a) a vacuum was applied to the top of the sample (with the bottom inlet open) or (b) compressed air was injected into the top (and hence out the bottom) or (c) the sample was left open at both ends and simply heated by the furnace. The samples were dry, except for the kerosene, when the experiments started, so the kerosene removal could be determined by sample weight loss.*

Figure 9 shows the results for the vacuum stripping experiments for sand and the 50/50 soil. Figure 10 shows the results for the air stripping experiments. Note the vacuum levels and air pressures used as given in Figures 10 and 11. Figure 11 shows the results for kerosene removal with only temperature elevation being used ($T = 100^{\circ}\text{C}$). In this case no vacuum or air was applied. In all cases the average of two runs was used and plotted. If the two runs had quite different results, a third run was performed for agreement and then the two consistent runs averaged.

It is seen from Figures 9 and 10 that the temperature of the soil is a most important variable in decontamination. Especially in the case of the 50/50 soil, a temperature of 100°C drastically raises the removal rate over that at ambient temperatures. However heat alone is insufficient to rapidly decontaminate the soil as is shown in Figure 11. There must be a forced air movement (either by vacuum or direct air injection) to allow the heat to act efficiently. That is, natural air flow is insufficient.

Figure 12 compares the steam stripping (at 5 psi steam pressure) and ambient temperature vacuum and air stripping techniques. It is seen that the steam stripping is clearly superior in removing the kerosene. Figure 13 compares the steam stripping and 100°C vacuum and air stripping techniques. The initial rate of kerosene removal is greater for the air and vacuum processes**, but the ultimate removal is better for steam stripping. The lower initial removal rate in the case of steam may be that initially the soil must be heated by the steam (via condensation) to reach 100°C. In the air and vacuum stripping experiments the furnace is at 100°C when the sample is put in and may reach 100°C faster than in the case of steam stripping experiments.

It is very important to note here that the vacuum used in the field will be very much lower than those used in these laboratory experiments. Hence a very biased comparison is being made here in favor of the vacuum technique. Also in the case of steam and air stripping it will be most difficult to heat separately the large soil masses encountered in the field to the elevated temperatures, a fact which also biases the comparison in favor of vacuum and air stripping.

Effect of Delay Times in Steam Stripping

If a dynamic decontamination method (such as steam stripping) is used for a certain time (not long enough to be essentially complete) and then stopped for a given "delay" period, what will be the consequences? If some of the less mobile contaminant can move to more mobile environs during the delay, is it possible that the new rate of removal will exceed that which was present immediately before the delay? An attempt has been made to look into this possible effect with controlled laboratory experiments.

*It is important to note that the weight change method cannot be used for steam stripping, for the water introduced adds extra weight to the sample. The output kerosene must be collected and monitored by volumetric separation.

**Again this may reflect an initial "pushing out" of the pollutant.

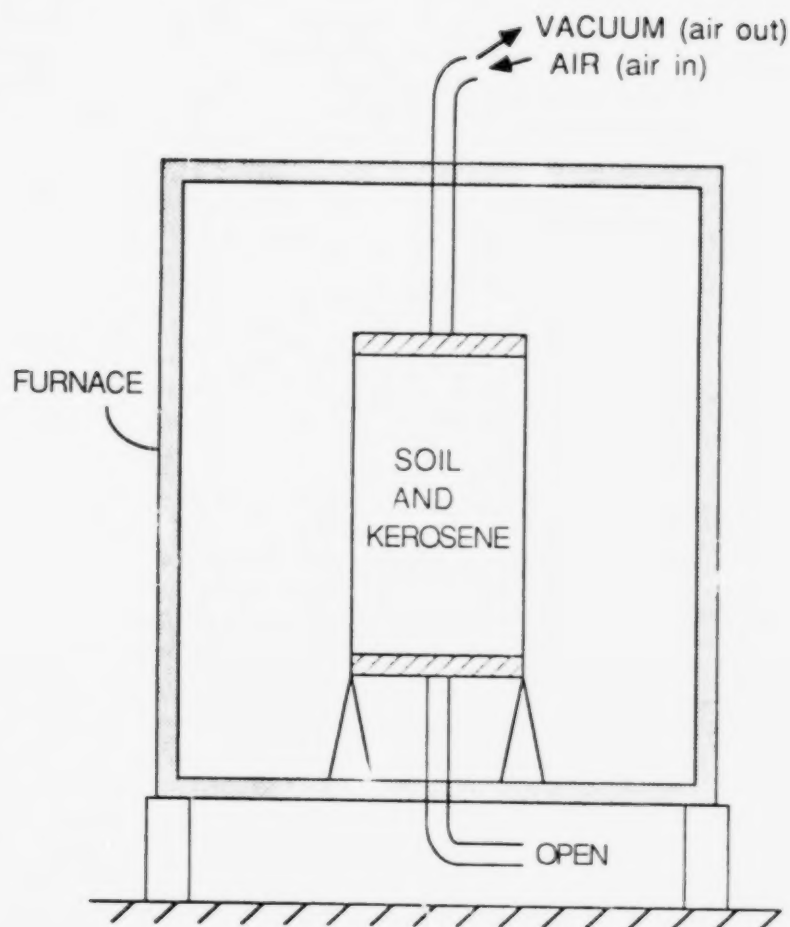


Figure 8 - Schematic Diagram of Apparatus
Used for Vacuum, Air and Heat Stripping

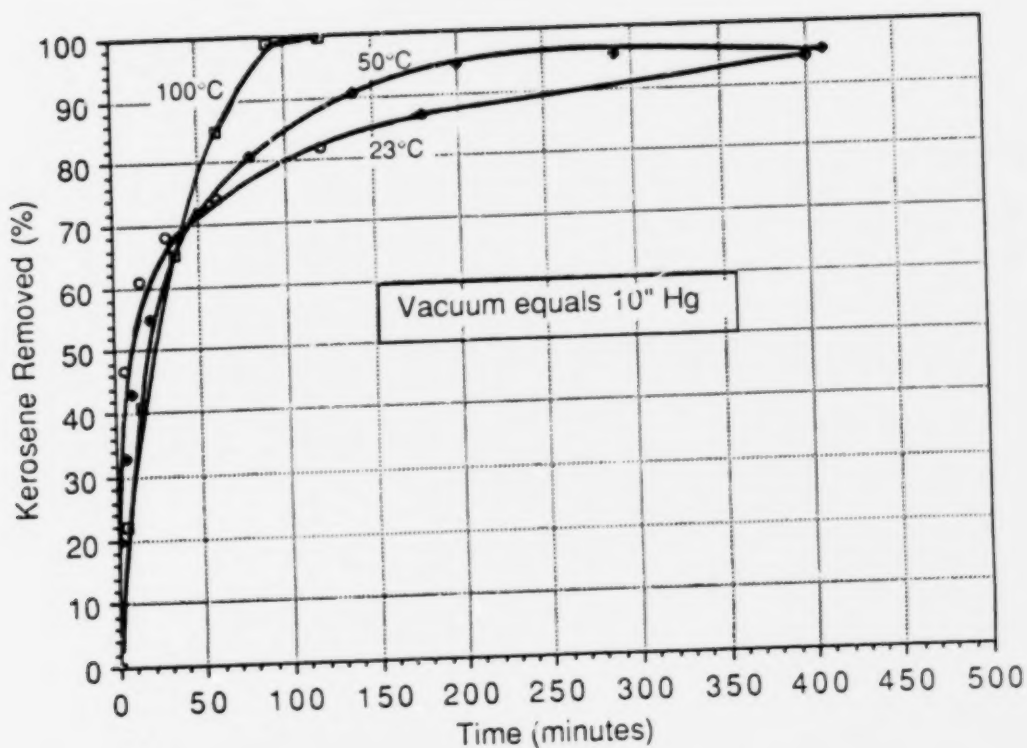


Figure 9(a) - Vacuum Stripping of 100% Sand

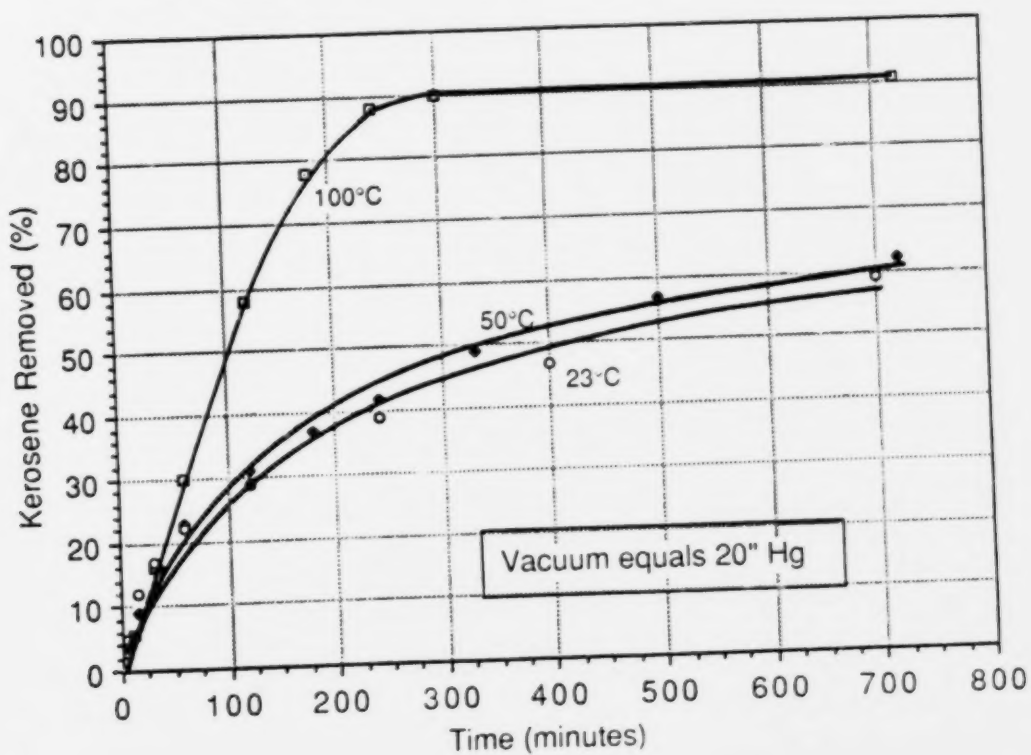


Figure 9(b) - Vacuum Stripping of 50/50 Soil

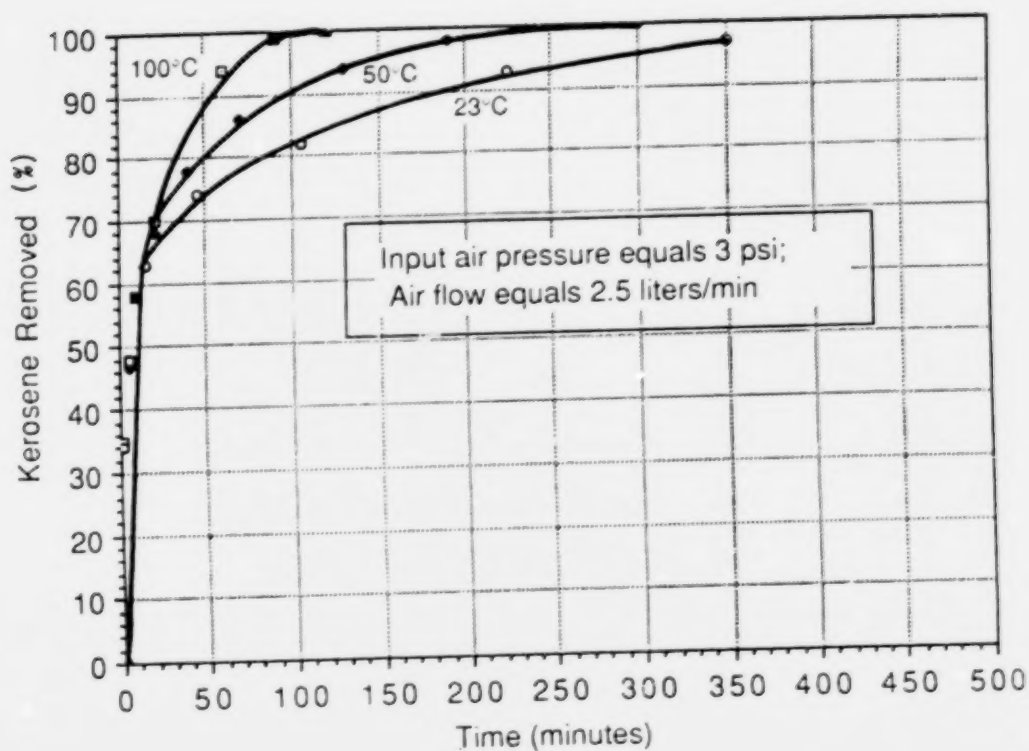


Figure 10(a) - Air Stripping of 100% Sand

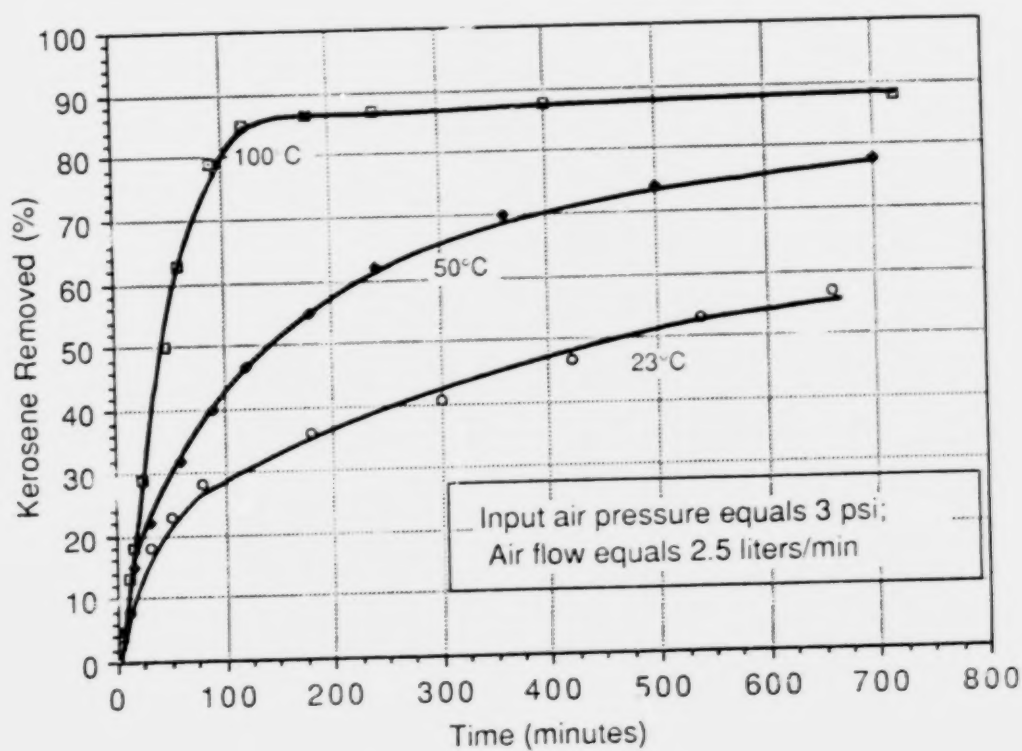


Figure 10(b) - Air Stripping of 50/50 Soil

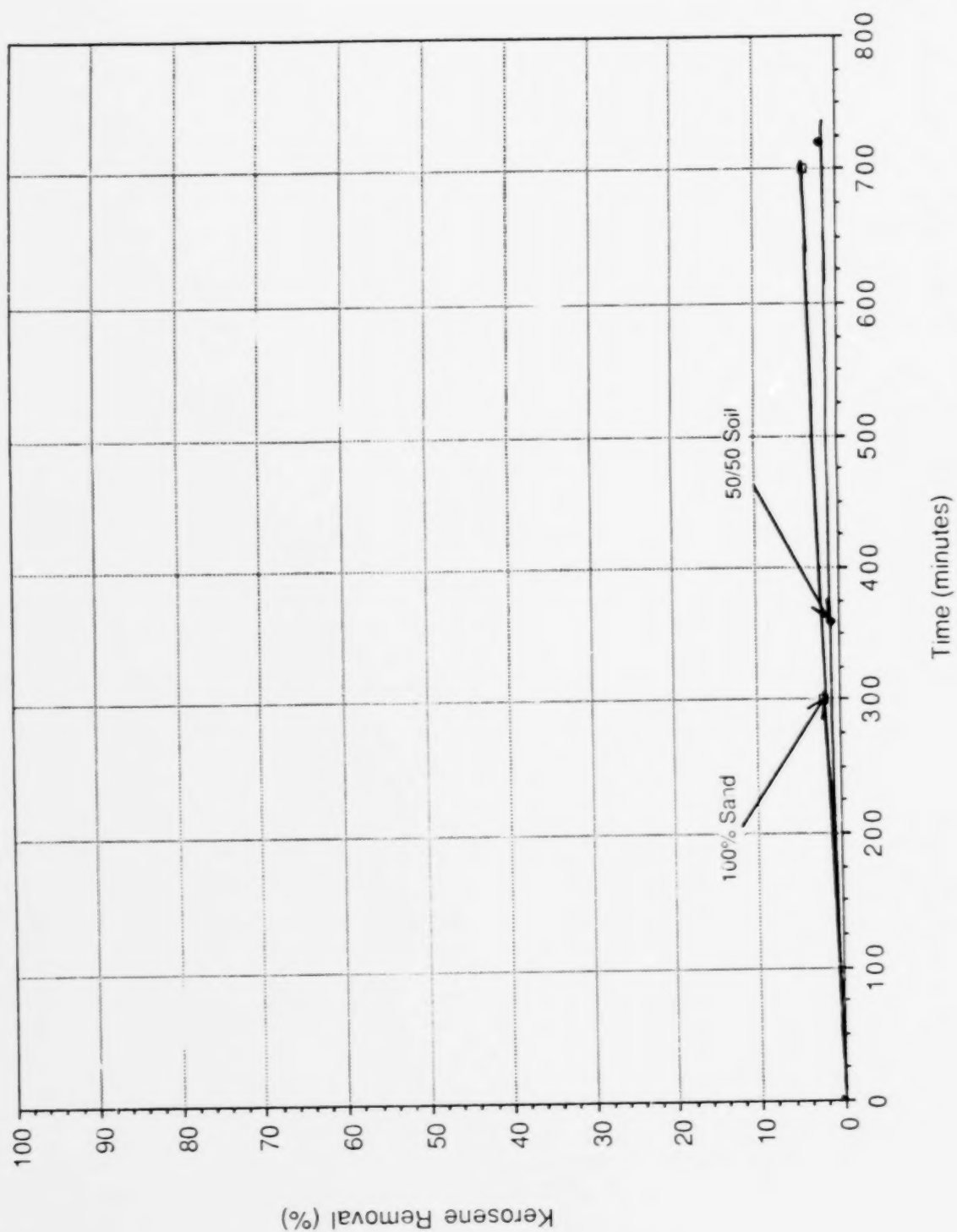


Figure 11 - "Heat Stripping Kerosene from 100% Sand and 50/50 Soil"

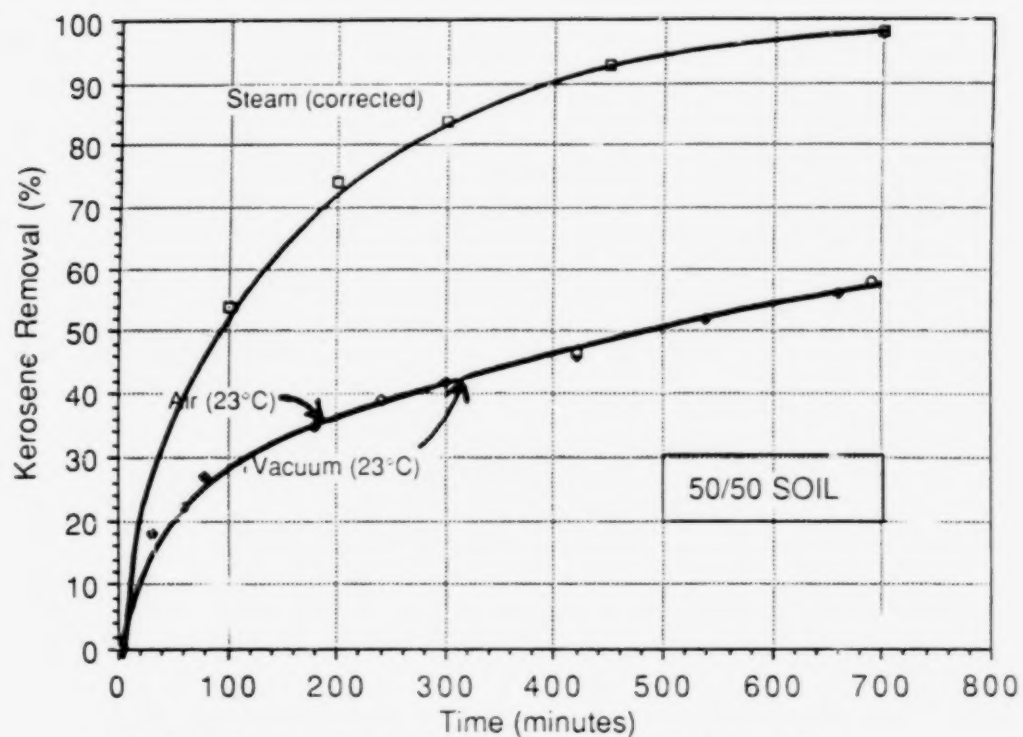


Fig 12 - Comparison of Decontamination Processes
(Vacuum and Air at 23° C)

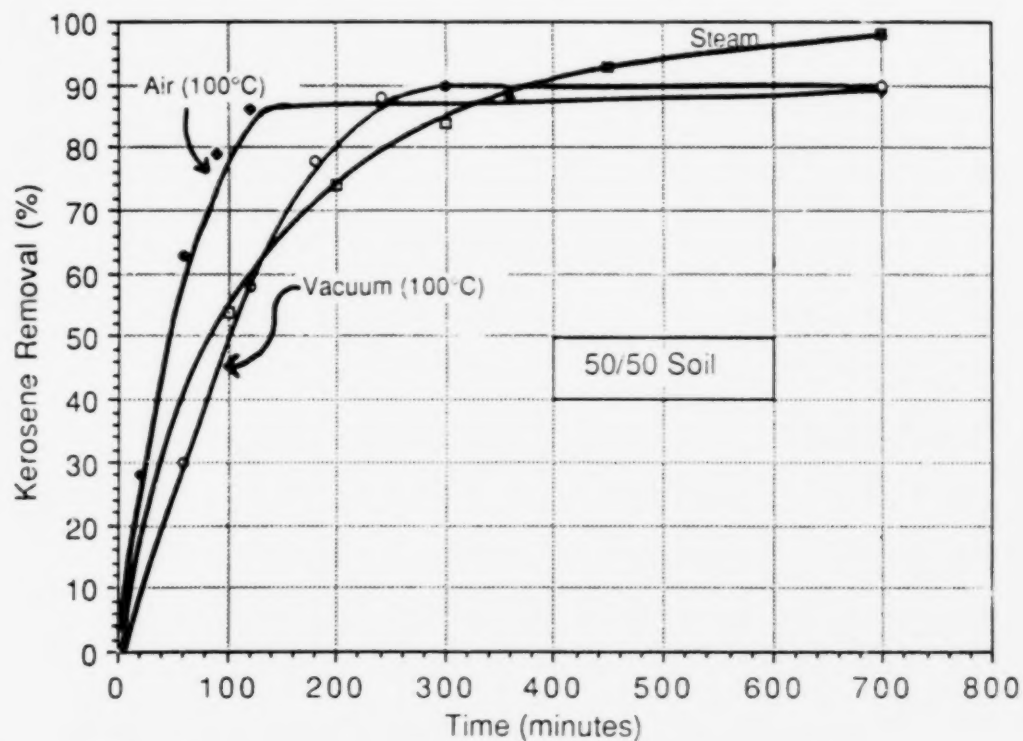


Figure 13 - Comparison of Decontamination Processes
(Vacuum and Air at 100° C)

Small cells, of the kind used in earlier reported work (3,8,9,10), were used. The soil was a 50% soil/50% silt mixture in which was mixed 20% kerosene. The material was vacuum-assisted steam stripped at a steam pressure of 5 psi and a vacuum of 20 inches of mercury for a period long enough to remove roughly 50% of the kerosene, at which time the rate of removal of kerosene had slowed considerably from the initial value. A number of samples were so prepared and then sealed and stored for subsequent use. Delay times of 15 and 50 days were used.

Unfortunately, for both the 15-day delay and the 50-day delay, the initial steam condensate upon resuming treatment was very brown-colored and non-separable, so the simple volumetric analysis cannot be performed. Some of the kerosene must have gone into the residual water during the delay. (No COD analysis was performed here.)

SUMMARY AND CONCLUSIONS

This paper presents the most recent results obtained in a laboratory project to ascertain the general viability of utilizing vacuum-assisted steam stripping to remove organic chemicals from a wide variety of soils. Our previous laboratory work had investigated steam flow in soils and the efficiency of removal of certain organic chemicals and mixtures from soils. Also a small scale demonstration of our proposed field set-up, which includes a unique easy-to-use geosynthetic cap assembly was performed.

The main thrust of the present work investigated the effect of differing steam pressures on the removal efficiency of a high boiling point organic compound from a soil with a permeability typical of many soils encountered in the field. To this end a new experimental apparatus had to be constructed. The results indicate that significantly larger amount of dodecane (b.p. 216°C) can be removed at 10 and 11.5 psi steam pressure than at either 3 or 5 psi. This has direct application to in-situ decontamination processes, if 10 psi can indeed be maintained at the subsurface steam entry point. The results may also have strong implications for vacuum-assisted steam stripping of excavated soils, where much, much higher steam pressures (and temperatures) could be maintained in a closed treatment vessel.

It should be mentioned that gas chromatography was the analytical method to determine the amount of chemical remaining in the soil. "Standard" methods of extracting the chemical from the treated soil were employed. There were indications from control work performed to find the accuracy of the method, that a significant amount of dodecane is bound to the silt particles.

Work was completed to ascertain the effect of sample temperature on the efficiency of vacuum-stripping and air stripping kerosene from sand and a 50% sand/50% silt soil mixture. It was found that raising the temperature of the soil sample to 100°C drastically enhanced the decontamination ability of both techniques. (The vacuum used here is of a much larger value than that used in the field.) The two methods were then somewhat competitive with steam stripping although steam stripping does ultimately remove more kerosene. Steam stripping is vastly superior to ambient temperature vacuum stripping and air stripping. Heat alone does not act as a good decontamination process — there must be some forced air movement to reach good removal rates. It, of course, will be extremely difficult to heat the soil in the field to these elevated temperatures for vacuum or air stripping.

A preliminary study was performed to ascertain if stopping the steam stripping for a given delay time would enhance the subsequent start up removal rate. Unfortunately, after delays of 15 and 50 days the steam condensate was very colored and could not be volume separated.

In general it appears that vacuum-assisted steam stripping is a very attractive method with which to decontaminate soils, and it works well on the hard-to-remove high boiling point organics.

SUGGESTED FUTURE WORK

It is important to use a clay and an organic fraction in the soil in future work. These will probably bind the organic chemicals and hence make them possibly more difficult to remove with the steam stripping, or any other process.

More high boiling point organic compounds, with varying properties, such as polarity, should be investigated. Vacuum and air stripping should be performed at lower vacuum levels and air pressures (much lower than those used herein), in order to more realistically compare steam stripping and these other decontamination techniques.

The analytical technique, used to determine the residual chemical remaining in the treated soil, should be investigated. A very thorough literature search should be undertaken in this regard. It may be necessary to work directly with soil chemists. (A different extraction method may be indicated.)

Delay time work should proceed with vacuum and air stripping.

It would seem appropriate at this time to "scale-up" the laboratory model field unit simulation work to ascertain some of the inevitable problems that always arise in applying a new technique. No prohibitive problems are foreseen due to its very good performance at the small laboratory size work, but "scale-up" is definitely warranted at this time.

ACKNOWLEDGEMENT

The Drexel authors wish to thank the Risk Reduction Engineering Laboratory of the U.S. EPA of Edison, New Jersey for their generous financial support of this work through Cooperative Agreement No. CR 513022.

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EVALUATION OF LIMITED-USE CHEMICAL PROTECTIVE CLOTHING USED FOR EPA SUPERFUND ACTIVITIES

by

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ABSTRACT

Limited- and single-use garments are used widely by EPA and EPA contractor personnel for protection from potentially hazardous liquids and solids at Superfund sites. Such garments are used in a wide variety of tasks and many hundreds of thousands of these garments are purchased each year. They are available from hundreds of distributors, in many different styles and configurations, and with significant differences in cost and quality. This study was undertaken as part of an overall effort to develop guidelines to ensure that the most appropriate product will be procured by those responsible for worker safety. Of particular concern were garment sizing and fabric strength and stiffness since field personnel frequently report that garments don't fit and that they tear, especially in the crotch and underarm areas and across the upper back.

Essentially all commercial fabrics used for limited-use chemical protective clothing (CPC) and two experimental fabrics were subjected to tests to measure breaking strength and flexibility. Based on these tests and the observations from the field, minimum values for breaking strengths of coated and uncoated fabrics, and maximum values for stiffness were deduced.

Several standards and specifications describing size and fit parameters for limited-use CPC were collected and reviewed. The two most significant conclusions were that (1) ANSI/ISEA Specification 101-1985 by itself was inadequate for EPA applications and (2) to be useful a sizing specification should relate garment size to body dimensions. From the

analysis, a sizing system was developed and used as a basis for a working version of the procurement guidelines and for recommendations to ANSI/ISEA and ASTM for modification of existing sizing standards.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The Environmental Protection Agency (EPA) has primary Federal regulatory responsibility for hazardous substance and hazardous waste (HS/HW) release, prevention, and clean-up operations in the United States. To address the risk to clean-up workers from HS/HW, the Occupational Safety and Health Administration (OSHA) promulgated 29 CFR 1910.120, *Hazardous Waste Operations and Emergency Response*, in 1988. This regulation requires personal protective equipment (PPE) to be provided for HS/HW activities.

PPE includes gloves, boots, garments, respirators, and so forth. These components are combined to provide four, progressively lower degrees of protection: Levels A, B, C, and D. Limited- or single-use garments are most commonly used as a part of Level C and, sometimes, Level B protection. The advantage of limited- or single-use clothing is that the costs and uncertainties of garment decontamination are obviated. Because they are usually disposed of after one or two uses, limited-use garments must be relatively inexpensive. Many cost less than \$20; although in some special cases, garments costing \$70-100 are disposed daily. Several hundred thousand, limited-use garments are used annually by the EPA and its Superfund contractors.

Typically the garment materials are composed of a woven or nonwoven fabric substrate onto which is laminated or coated a continuous film of plastic to provide a barrier to liquids and vapors. Nonwoven fabrics without the film are sometimes used when the HS/HW is a solid. The material is stitched, adhesively bonded, or heat-welded together to produce a garment. The garment may or may not have pockets, attached hood and boots, elastic bands at the wrists and ankles, and so forth. The garments are worn over street clothing, which can range from shorts and a T-shirt in hot climates to bulky jackets and heavy trousers in cold climates. At present the most commonly used limited-use garments are based on Tyvek® 1422 spunbonded polyolefin, a porous, nonwoven fabric (Du Pont)¹. Because it is porous, the Tyvek 1422 is laminated or coated with polyethylene film or Saranex 23-P® film (Dow). Recently, however, other products have been introduced with claims of greater durability or better resistance to chemicals. These include Barricade® (DuPont), Responder® (Lifeguard), and Chemrel Max® (Chemron).

¹ Mention of tradenames or commercial products does not constitute endorsement or recommendation for use.

PURPOSE

This study was undertaken as part of an overall effort to develop guidelines to ensure that the most appropriate limited-use garment can be procured by those responsible for worker safety. Of particular concern were garment sizing and fabric strength and stiffness since field personnel frequently report that garments don't fit and that they tear, especially in the crotch and underarm areas and across the upper back.

DESCRIPTION OF THE PROBLEM

EPA and EPA contractor personnel report limited-use CPC tears, especially coveralls of Tyvek 1422. Coveralls constructed of Tyvek 1422 coated with polyethylene (PE) or laminated to Saranex 23-P are more durable, but some failures occur. Kleenguard® (Kimberly-Clark) garments are reported by some field personnel to be less prone to tearing than Tyvek 1422, but the fabric is not available in coated forms. Tearing most frequently occurs in the crotch and underarm areas and across the upper back. Tearing may be due to insufficient fabric or seam strength or incorrect sizing.

Workers also report that garments are tight in the hood, chest, back, seat, armholes, and thighs, especially when worn over cold weather clothing. Tightness may be due to incorrect sizing or that the worker was not wearing the correct size garment. Many field workers wear oversize garments and "field tailor" them with duct tape. Women and large men have the worst fit problems.

Workers reported that many of the newer fabrics, while apparently stronger and having better chemical resistance, are stiffer and, consequently, less comfortable to wear than garments based on Tyvek 1422 or Tyvek 1422/PE or Tyvek 1422/Saranex 23-P.

Field personnel reported that cost is a very significant factor in the selection of fabrics and garments. It appears that there is a price point between \$20 and \$40 above which disposal after use is prohibitive and discouraged in actual practice.

PHYSICAL PROPERTIES OF LIMITED-USE FABRICS

PROCEDURES

To gain insights into the strength and flexibility characteristics of the fabrics of limited-use garments, specimens of seventeen fabrics were subjected to three standard tests.

ASTM D1682 - Breaking Load and Elongation of Textile Fabrics. In this test, a continually increasing load is applied longitudinally to the fabric specimen. The load at which the fabric breaks is the test result.

ASTM D1388 - Stiffness of Fabrics. In this test, a strip of fabric is slid in a direction parallel to its long dimension, so that its end projects from the edge of a

horizontal surface. The length of fabric overhanging the edge (divided by two) when the end of the fabric is at a specified angle to horizontal is the test result.

ASTM D3776 - *Mass Per Unit Area (Weight) of Woven Fabric*. In this test, the weight of a specified area of fabric is measured.

For ASTM D1682 and ASTM D1388, tests were performed with the required number of specimens from two, perpendicular directions on the fabric. The results averaged since machine and cross directions could not be distinguished for all fabrics.

RESULTS

Results are presented in Table 1.

Tyvek 1422 had the lowest breaking strength of any fabric tested, 8.5 pounds, although the value is not significantly different from those for Kleenguard (9.7) and Enhance (8.8). The most commonly used coated fabric, Tyvek 1422/PE, had a breaking strength of 13.3 pounds; Tyvek 1422/Saranex 23-P was essentially the same at 13.6 pounds.

The experimental fabrics, Tyvek 1443/PE and Tyvek 1445/PE, showed breaking strengths of 12.3 and 14.9 pounds, respectively.

The uncoated fabrics generally exhibited the highest flexibility, with bending lengths ranging from 1.2 to 1.9 inches (lower bending lengths indicate greater flexibility). The coated, nonwoven fabrics were generally stiffer, with bending lengths ranging from 1.5 to 4.4 inches. Three of the coated, nonwoven fabrics had curls that made them inappropriate for the test.

The coated woven fabrics, Chemtex, Chemgard®, and Neonyl®, were the strongest and had bending lengths that spanned 0.9 to 2.8 inches. The coated woven fabrics, however, have much higher weights and garments fabricated from them are probably too expensive for use as a day-in, day-out, disposable garment.

DISCUSSION

The fabrics can be divided into two stiffness categories: bending lengths less than or greater than 2 inches. One could infer from subjective comments from field personnel that acceptable garments should be constructed from fabrics having a bending length less than 2 inches. This is supported by comments from the field that Tyvek 1422/Saranex 23-P garments are the stiffest fabrics that are considered acceptable. Also based on comments from the field, the minimum acceptable breaking strength may be in the range of 9-14 pounds. Information gathered from the field in this study would suggest that the strength of Tyvek 1422 is less than acceptable, that of Tyvek 1422/PE is marginal, and that of Kleenguard and Tyvek/Saranex 23-P are acceptable.

TABLE 1. PHYSICAL CHARACTERISTICS OF LIMITED-USE
CHEMICAL PROTECTIVE CLOTHING FABRICS

Fabric (Source)	Type ‡	Weight*	Breaking strength**	Bending length†
Tyvek 1422 (Du Pont)	NW	1.24 (0.15) ⁺⁺	8.5 (1.7)	1.2 (0.6)
Kleenguard (Kimberly-Clark)	NW	1.85 (0.1)	9.8 (1.3)	1.6 (0.2)
Enhance (Abandaco)	NW	1.88 (0.2)	8.8 (3.6)	1.9 (0.6)
Tyvek 1422/PE (Du Pont)	CNW	2.18 (0.15)	13.3 (1.6)	1.8 (0.7)
Tyvek 1443/PE (Du Pont)	CNW	2.14 (0.2)	12.3 (0.3)	1.8 (0.6)
Tyvek 1445/PE (Du Pont)	CNW	2.23 (0.25)	14.9 (5.0)	2.1 (1.1)
Encase II (Abandaco)	CNW	2.33 (0.3)	12.7 (2.7)	1.5 (0.6)
PP/Saranex 23-P (Abandaco)	CNW	3.53 (0.25)	13.1 (3.4)	1.9 (0.3)
Tyvek 1422/Saranex 23-P (Abandaco)	CNW	3.60 (0.2)	13.6 (1.4)	1.7 (0.6)
Chemtuff (Chemron)	CNW	3.60 (0.35)	46.4 (6.2)	NA†
Chemrel (Chemron)	CNW	4.08 (0.45)	21.3 (6.6)	NA
Chemrel Max (Chemron)	CNW	5.19 (0.6)	38.9 (7.4)	NA
Barricade (Du Pont)	CNW	6.39 (0.45)	28.2 (6.0)	2.4 (1.2)
Responder (Lifeguard)	CNW	8.23 (0.9)	38.1 (5.7)	4.4 (0.7)
Chemtex (Bata-Sijal)	CW	9.52 (1.2)	101.6 (12.4)	0.9 (0.1)
Chemgard (Rainfair)	CW	10.40 (1.1)	65.6 (8.1)	1.6 (0.6)
Neonyl (Rainfair)	CW	15.19 (0.6)	117.6 (17.0)	2.8 (0.5)

* ASTM D 3776, option C; ounces/square yard.

** ASTM D 1682, 5 inch/minute constant-rate-of-extension; pounds

+ ASTM D 1388, option A, inches

++ Number in parentheses is standard deviation

† Test not applicable; fabric had permanent curl.

‡ NW = nonwoven; CNW = coated or laminated nonwoven; CW = coated woven

SIZING AND FIT OF LIMITED-USE GARMENTS

ANSI/ISEA², *Standard 101-1985, Men's Limited-Use and Disposable Protective Coveralls-Size and Labeling Requirements*, specifies minimum dimensions for five sizes of coverall. See Table 2. Compliance with the specification is voluntary.

TABLE 2. ANSI/ISEA 101-1985 MINIMUM REQUIREMENTS

Size*	Chest	Leg inseam	Sleeve outseam	Body length	Sleeve opening	Leg opening	Front opening length
Small	21-1/2	27-1/2	31-1/2	35	6-1/2	9-1/2	29-1/2
Medium	23-1/2	28	32-1/2	36	7	10	29-1/2
Large	25-1/2	29	33-1/2	37	7	10	30
X-Large	27-1/2	29-1/2	35	38-1/2	7	10	30-1/2
XX-Large	29-1/2	30	36-1/2	39	7	10	31

* All dimensions in inches.

In the summer of 1987, two types of coveralls were obtained from five manufacturers of limited-use coveralls and measured according to the instructions of ANSI 101-1985. The results are shown in Table 3. None of the Tyvek 1422 garments and two the Tyvek 1422/Saranex 23-P completely met all the dimensions of the ANSI/ISEA standard. In a few cases, the garments would appear to be significantly below the minimum dimensions; however, the deficiencies could be considered minor in most cases. From 1987 to present, the major manufacturers were increasingly claiming adherence to the ANSI/ISEA specification. Failures due to tearing, however, continued to be reported by EPA and EPA field personnel. This observation suggests that, while manufacturers may have been meeting the minimum dimensions of the specification, the specification may be inadequate.

²ANSI - American National Standards Institute; ISEA - Industrial Safety Equipment Association.

TABLE 3. MEASUREMENTS OF LIMITED-USE COVERALLS

Dimension	Minimum ANSI/ISEA 101-1985	Tyvek 1422 Manufacturer					Tyvek 1422/Saranex 23-P Manufacturer				
		1	2	3	4	5	1	2	3	4	5
Chest	25.5*	26.2	28.8	25.2	26.8	27.0	26.4	26.0	29.2	28.0	27.0
Leg inseam	29.0	29.0	30.2	27.0	29.2	29.2	26.5	28.5	30.2	27.0	28.5
Sleeve outseam	33.5	34.5	34.0	3.5	33.0	36.0	33.4	33.8	36.2	37.0	40.0
Body length	37.0	36.1	37.5	40.2	40.2	35.0	40.7	36.8	39.0	43.0	38.8
Sleeve opening	7.0	7.5	6.2	7.2	8.2	6.8	7.9	7.0	7.8	7.2	6.2
Leg opening	10.0	11.0	9.0	10.2	10.8	9.5	11.0	11.0	11.5	11.5	11.5
Front opening	30.0	29.8	28.0	29.8	30.8	28.0	28.9	30.0	30.2	26.5	29.5
Hood width	**	9.6	12.75	11.0	9.0	11.0	11.0	11.0	1.75	10.0	9.8
Hood length	**	14.7	14.0	15.3	15.0	14.75	15.2	15.5	14.5	15.5	15.5

* All measurements in inches.

** Not a requirement.

Consequently, in order to meet the objective of the study (i.e., guidelines that would aid the process of procuring acceptable garments), attention was directed towards finding a basis for recommending modifications to the ANSI/ISEA specification. The effort was focussed on other directly related or pertinent standards. Three were identified:

MIL-C-29133A -- *Coveralls, Disposable, General Purpose*
MIL-C-87069A -- *Coveralls, Disposable*
BS 5426:1987 -- *Workwear and Career Wear*

The British Standard (BS) was unique in that it related garment sizes to body dimensions. While such an approach is common for commercial clothing (e.g., consider the size/body dimension charts in mail order clothing catalogs), it has not been practiced in the area of chemical protective clothing. The British Standard also contained more sizes as means for increasing the likelihood of having garments that fit a wider range of the population.

Other observations and conclusions based on the review of the standards and the technical literature and the experience of the authors are:

- The current range of 5 sizes should be expanded to 6 sizes to provide a better fit range, especially for women and large males. Dimensions for these 6 sizes are proposed in Table 4.
- The field data suggests that insufficient back body length is included in present coverall designs. Tearing under the arm may be related to inadequate back width and armhole width. Additional back length and ease for the armhole is required to fit over winter clothing.
- Additional sleeve outseam and leg inseam length will increase the range of fit for tall workers.
- A range of sleeve openings will keep excess bulk from hindering smaller sizes and allow easier donning and doffing for larger males.
- An increase in leg opening size will provide a wider range of fit, especially when donned over safety shoes.
- An increase in the difference between front and back width will increase range of motion, especially for the arms when reaching.
- An increase in the range of front opening lengths will ease donning for larger males.

TABLE 4. PROPOSED MINIMUM FINISHED DIMENSIONS FOR
LIMITED-USE COVERALLS

Dimension *		Size					
		XS	S	M	L	XL	XXL
A.	BACK BODY LENGTH	38	39	40	41	42	43
B.	FRONT BODY LENGTH	33	34	35	36	38	40
C.	ARMHOLE WIDTH	11	11	12	13	14	15
D.	SLEEVE OUTSEAM	32	32	33	34	35	36
E.	SLEEVE OPENING	6	6	7	7	8	8
F.	FRONT CHEST	22	23	24	26	28	30
G.	BACK CHEST	23	24	26	29	32	34
H.	LEG INSEAM	28	29	30	31	32	33
I.	LEG OPENING	10	10	11	11	12	12
J.	FRONT OPENING LENGTH	29	29	30	30	31	32
K.	HOOD LENGTH	16	16	17	17	18	18
L.	HOOD DEPTH	10	10	12	12	14	14
M.	NECKLINE LENGTH	16	16	18	19	20	20

* All measurements in inches.

- ANSI/ISEA 101-1985 does not currently include hood dimensions, however, hoods are considered desirable for EPA activities, and must fit when worn over hard hats. Hood opening length and hood depth requirements are required.
- Neckline length requirements are needed to assure fit when worn over winter clothing.
- The procedures for measuring the dimensions of a garment should be changed from that of ANSI/ISEA 101-1985 to those proposed in Table 5.

In the proposed sizing system, extra-small and small have been optimized for females, medium represents a compromise for larger females and smaller than average males, large represents a slightly larger than average male, and extra-large and extra-extra-large are optimized for upper-percentile males. Size extra-extra-large should fit a 95th percentile worker wearing winter clothing in a temperate climate zone.

CONCLUSIONS

Improvements described for both fabrics and coverall sizing are a starting point for continuing efforts to provide improved protective clothing for EPA hazardous waste workers and guidelines for its procurement.

TABLE 5. PROPOSED LIMITED USE COVERALL
MEASUREMENT PROCEDURES

-
- A. BACK BODY LENGTH. Measure from the top of the neckline at the center back collar seam to the crotch seam.
 - B. FRONT BODY LENGTH. Measure from the top of the neckline at the center back point to the crotch seam with the coveralls flat and front side up.
 - C. ARMHOLE WIDTH. Establish a line from the base of the armhole which is parallel to the center front. Measure up from the armhole base to the top of the sleeve with the coveralls stretched flat.
 - D. SLEEVE OUTSEAM. Measure from the center back point to the top of the sleeve at the wrist edge.
 - E. SLEEVE OPENING. Flatten sleeve at wrist end, completely stretching elastic if present. Measure from one folded edge to the other.
 - F. FRONT CHEST. Measure from the base of the armhole across the front chest to the base of the other armhole. If there is no underarm seam on either sleeve or body of coverall, lay the sleeve and body of coverall at an angle where both are flat and establish an underarm point at the juncture of the sleeve and torso.
 - G. BACK CHEST. Measure from the base of the armhole across the back to the base of the other armhole, including all of the fullness that lies between these two points. If there is no underarm seam on either sleeve or body of coverall, lay the sleeve and body of coverall at an angle where both are flat and establish an underarm point at the juncture of the sleeve and torso.
 - H. LEG INSEAM. Measure from the crotch seam down the leg inseam to the bottom edge.
 - I. LEG OPENING. Flatten the leg at the ankle end, completely stretching elastic if present. Measure from one folded edge to the other folded edge.
 - J. FRONT OPENING LENGTH. Measure from the center back collar base to the bottom of the front opening with the coverall flat and front side up.

(continued)

TABLE 5 (continued)

-
- | | |
|----|--|
| K. | HOOD OPENING LENGTH. Flatten the hood along the center seam so that the sides are superimposed. Measure on a flat vertical line that extends upward from the neckline seam to the highest point on the top of the hood. |
| L. | HOOD DEPTH. Flatten the hood along the center seam so that the left and right sides are superimposed. Measure on a horizontal line from the center front (face) edge to the back of the hood at the point of greatest depth. |
| M. | NECKLINE LENGTH. With front of coverall facing up, stretch neckline seam flat. Measure from one end of seam to the other. |
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Methods to Evaluate the Stress Crack Resistance of
High Density Polyethylene FML Sheets and Seams

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Abstract

The stress crack resistance of high density polyethylene (HDPE) flexible membrane liner sheets and seams is evaluated using three different testing methods. The sheet materials are evaluated using the bent strip constant strain test (ASTM D-1693) and the notched constant load test (NCLT). The seams are evaluated using the seam constant load test (SCLT). The experimental procedures used in each of these methods is described.

In addition, the effects of elevated temperature on the stress crack resistance of HDPE sheet is discussed. The surface temperature of the FML's can be reduced significantly by using some type of cover materials, thereby reducing the stress cracking potential of the FML's.

Introduction

The stress cracking of high density polyethylene (HDPE) geomembrane sheet and seams is of concern due to a few failures at surface impoundments where the FML's were exposed to the ambient environment. Presently, only one quality control test method, ASTM D-1693(1), is used to evaluate the stress cracking of HDPE sheet materials used as FML's. However, the currently used test conditions may not be able to distinguish the stress cracking performance between different materials. It is felt that more quantitative and challenging test methods would help to ensure that the best possible materials are being utilized. It should also be noted that there is no current test method used to evaluate FML seams as to their stress crack resistance.

In addition to a qualification of the HDPE materials, the ambient

environment where the FML will be utilized should also be considered. In some applications, such as surface impoundments, the FML is fully exposed to ambient environments along the runout length and down the slope to the liquid level. The surface temperature of the FML becomes a concern, since temperature is one of the acceleration factors associated with aging of HDPE liners and stress crack propagation. Minimizing the surface temperature and direct sunlight exposure will probably extend the performance of these materials.

This paper focuses on four separate topics, each of which will be independently presented. They are as follows:

- Bent strip test for HDPE sheet materials (ASTM D-1693).
- Notched constant load test (NCLT) for HDPE sheet materials.
- Seam constant load test (SCLT) for HDPE seams.
- Temperature reduction of exposed HDPE liner materials.

Suggested procedures and recommendations on all four topics are included.

Bent Strip Test (ASTM D-1693)

The ASTM D-1693 bent strip test entitled "Environmental Stress-Cracking of Ethylene Plastics" is the only test method currently used by FML manufacturers to evaluate the susceptibility of polyethylene sheet material to stress cracking. The procedure uses small specimens (38mm x 13mm) which are taken directly from the manufactured sheet. A central notch 20mm long and from 0.30 to 0.40 mm deep is introduced along the length of each of the ten test specimens. The test specimens are then bent 180° and held in the flanges of a small channel. The entire assembly is immersed in a surface-active agent at an elevated temperature. Figure 1 shows a notched specimen, the channel holder and a glass beaker which can be used to incubate the set of ten replicate specimens. Note that the test specimen in this configuration results in a constant tensile strain on the outside surface. If cracks are observed on the surface before an arbitrarily defined length of time, the sheet material is considered to be sensitive to stress cracking. When cracks occur, they generally develop at the sides of the controlled notch near the top of the arch, growing towards the edge of the specimen at approximately right angles to the notch. They sometimes break through the entire thickness of the specimen in a brittle mode indicative of poor stress crack resistance.

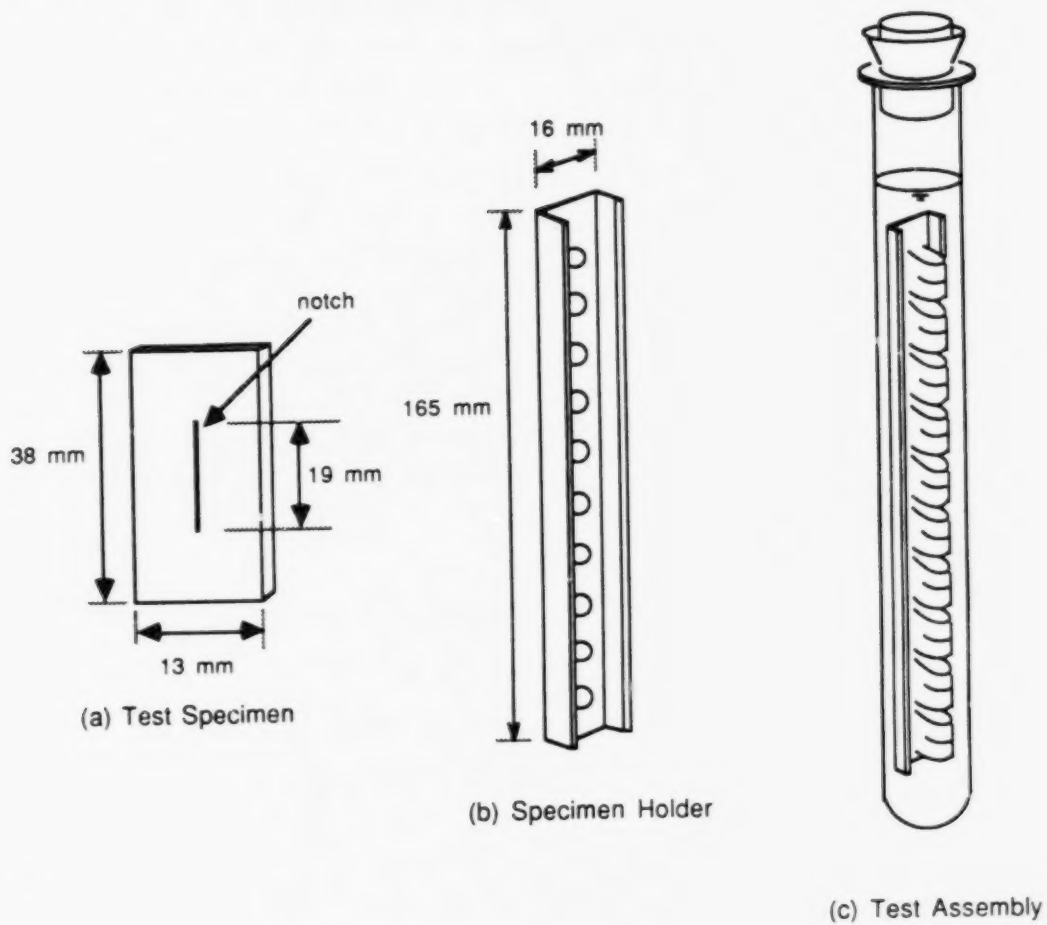


Fig. 1 - Test setup for ASTM D-1693 bent strip test

Since this test is accelerated by both the surface-active agent and the elevated temperature, the conditions of these two factors must be carefully considered. A National Sanitation Foundation (NSF) Committee has recommended in their Standard #54 that the conditions of the test be 100% Igepal as the surface-active agent and 100°C temperature. They also stipulate that no failures occur within a 500 hours test duration. It must be recognized, however, that these conditions are not extremely severe, and each of the conditions is discussed in following:

- Concentration - The viscosity of 100% Igepal solution is very high. The liquid is unlikely to penetrate completely into the notch and expand the defects so as to assist in the crack propagation. A lower viscosity solution with higher penetration capability will facilitate the crack growth more if there is such a tendency.
- Temperature - The 100°C test temperature is very close to the melting point of HDPE which is 124°C. Thus stress relaxation in the test specimens can occur much easier than at lower temperatures. In addition, for test solutions which contain water, the testing temperature must be lower than 100°C to minimize the evaporation of water.
- Time - The duration for an acceptable test is a difficult decision. If the defined testing time is too short, it certainly cannot demonstrate the true property of the material. On the other hand, a long period of time may not necessarily be a sensible choice because of polymer stress-relaxation. Indeed, there may not be any tensile stress remaining in the specimen after a long period of testing time. The presently defined 500 hours testing time is probably too short, since cracking has been observed in some tests at times between 500 and 1000 hours.

The recently reconvened NSF #54 Committee has also addressed these details of the test and its current deliberations are focused around the use of 10% Igepal in 90% tap water, at 50°C, for 1000 hours. They also recommended that no failure should occur in any of ten test specimens which are to be taken equally from both the machine and cross-machine directions of the sheet material.

Notched Constant Load Test (NCLT)

This test is intended to evaluate the stress cracking resistance of FML sheets under constant load. As such, it does not allow for stress-relaxation to occur as in the previous test. For this reason alone, the test is a more severe indicator of the stress crack performance of HDPE sheet materials.

The test itself has references dating back to 1960(2), which resulted in an ASTM test procedure that was designated ASTM D-2552. It has since been dropped by ASTM due to inactivity in the use of this standard. The test used dumbbell shaped specimens at various constant loads which were equal to percentages of the yield strength of the material. The specimens were immersed in a surface-active agent at an elevated temperature. A schematic diagram of a 20 station test unit is shown in Figure 2. Each station was individually equipped with a timing light which shuts off when a given amount of deformation of the specimen occurred. Thus the test had three possible concluding states:

- elastic state - where the light never shuts off up to an arbitrary time limit, e.g. 1000 hours
- plastic state - where the light shuts off due to plastic elongation of the specimen
- cracked state - where the light shuts off due to brittle cracking of the specimen

Unfortunately, this test as written required an extremely long period of time (= 10,000 hours) to conclude. Furthermore, the results were very random. This was because there was no controlled imperfection within the specimens. The crack initiation in the individual test specimens was dependent upon the material's own defects which varied randomly from one specimen to another.

A modification of this test to alleviate the above disadvantages is proposed. The specimens to be used in this new test are made according to ASTM D-1822 which has a constant central section 120mm long and 30mm wide. A controlled notch is then introduced into one side of the surface to a depth of 20% of the thickness of the specimen. Figure 3 shows the schematic diagram of a notched test specimen. To distinguish the new test from the older one, this test is designated a notched constant load test, or "NCLT". The details of specimen preparation have been fully described in a previous paper(3).

Test specimens are taken parallel to the cross machine direction of the

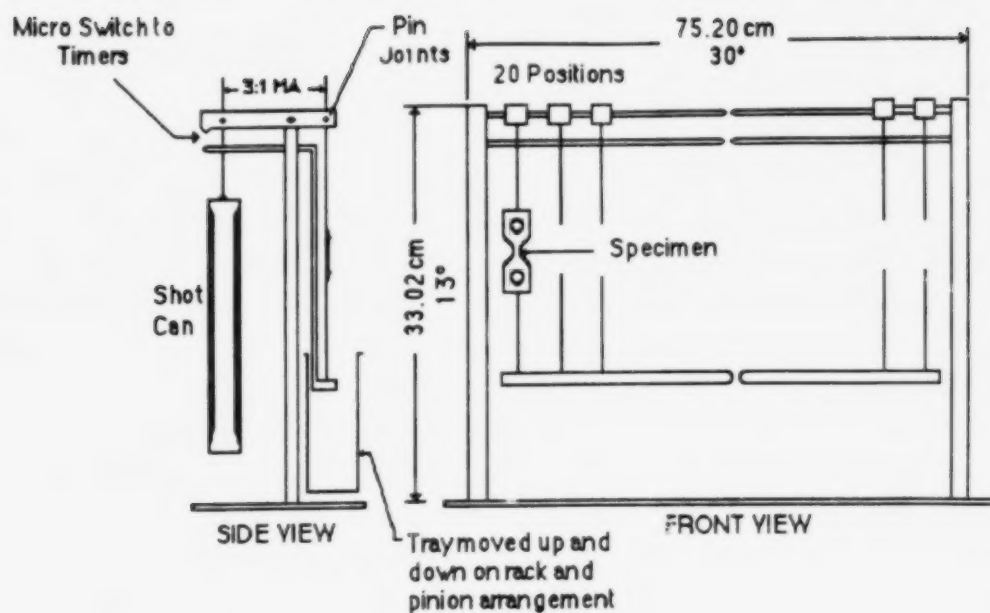


Fig. 2 - Constant stress loading apparatus consisting of twenty specimen test positions

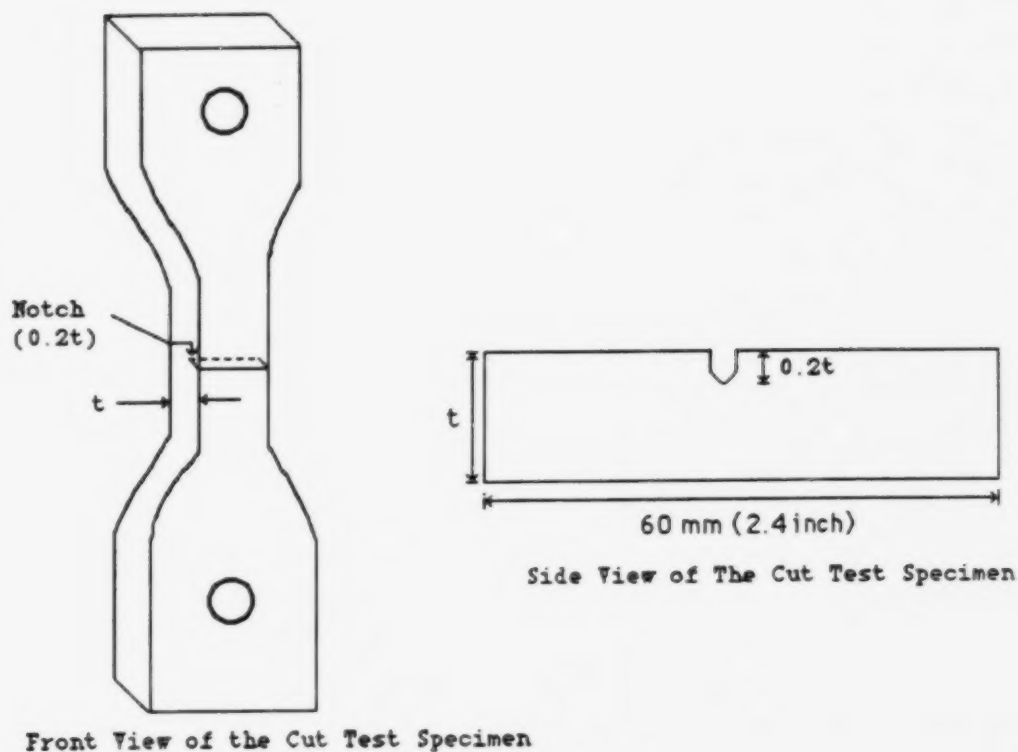


Fig. 3 - Schematic diagram of Notched test specimen for notched constant load test (NCLT)

sheet and then notched perpendicular to the specimen length, i.e. in the machine direction of the sheet. Past testing has shown this to be the most sensitive direction for stress cracking. The notched specimens are then prepared with grommets in their end tabs and placed in the test device which is capable of testing up to 20 specimens simultaneously as was shown in Figure 2.

The specimens are subjected to a predetermined constant load while immersed in a 10% Igepal/90% tap water solution at a temperature of 50°C. The load levels range from 25% to 70% of the yield stress of the material at 50°C. The load increments are at even 5% intervals. The failure time of the specimens is automatically recorded to the nearest 0.1 hour. After the test is completed (the time of which varies, but is at least long enough to obtain brittle failures in some of the specimens), the experimental data is presented by plotting the applied stress against the failure time on a log-log scale. The data points can be visually separated into two linear regions. The initial region consists of ductile failures and the terminal region consists of brittle failures, see Figure 4. The time corresponding to the point at which the lines intersect is called the ductile-to-brittle transition time, and is designated as " T_t ".

The transition time of the FML sheet has been shown to be very sensitive to the properties of the material and probably to the manufacturing process as well. The results presented in previous paper⁽³⁾, and reproduced in Table 1, indicate that there is a wide range of transition times, from 4 to 600 hours, between different HDPE sheets. Also note that there is a correlation between the transition time and the bent strip test results, particularly for the poor stress cracking resistance materials. However, for materials with transition times greater than 100 hours, the bent strip test results were the same. Hence the bent strip test is a qualitative test, whereas the NCLT is a quantitative one.

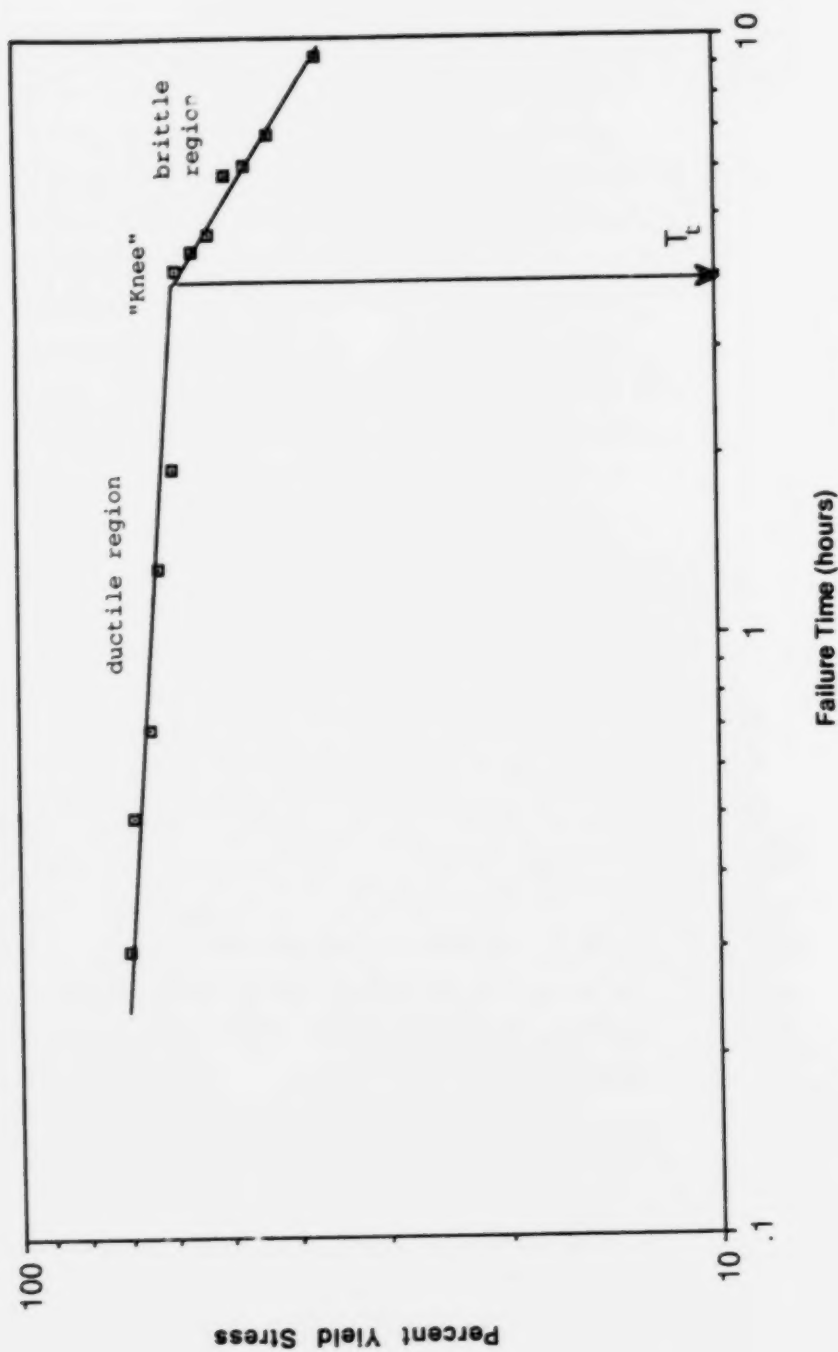


Fig. 4 - Ductile-Brittle curve of a specific polyethylene liner, showing "knee" shaped transition. Testing was performed at 50°C and 10% igeal solution.

Table 1 - Results of Bent Strip Test and Ductile-to-Brittle Transition Times for Five Different Polyethylene Sheets (from Ref. 3)

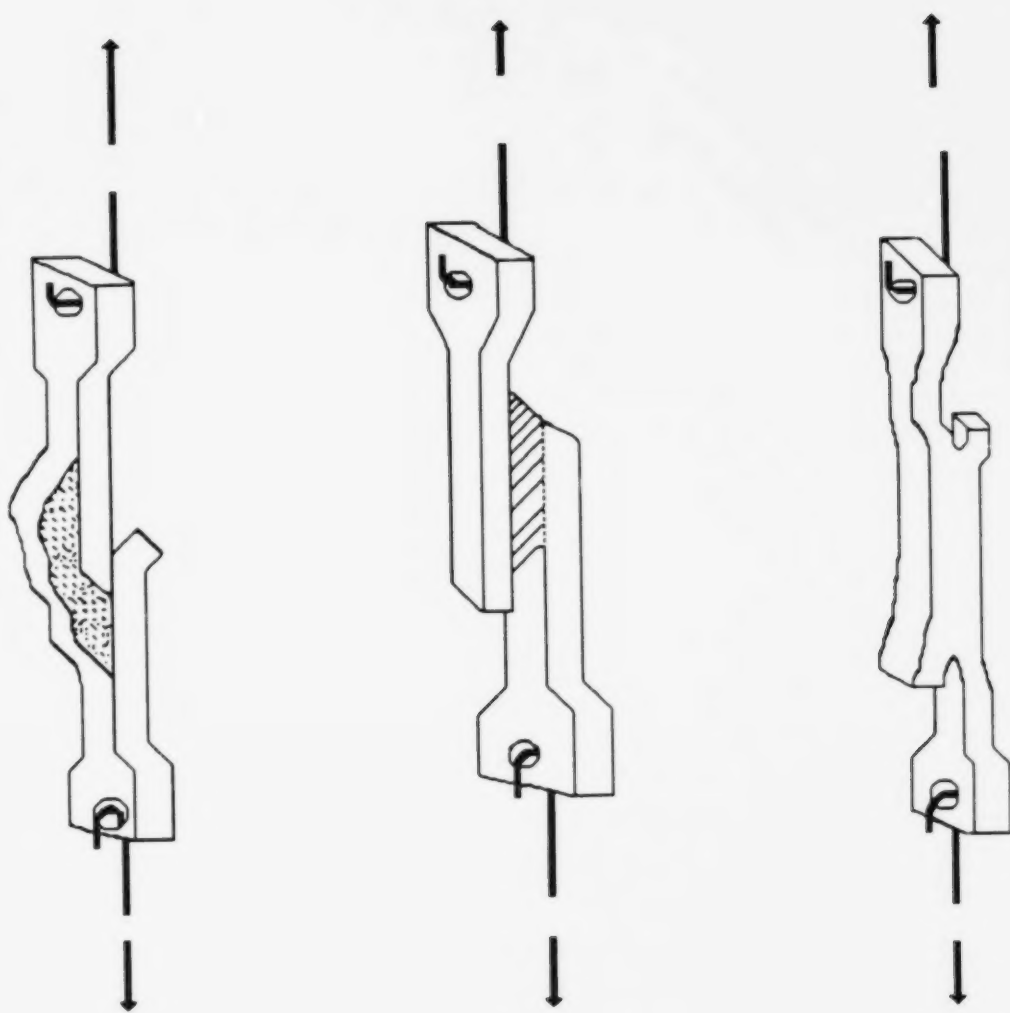
Materials	Bent Strip Results (no. failure/ hours of test)	Transition Time (hours)
S-1	9/700	4
S-2	6/700	6
S-3	0/2000	600
S-4	5/2000	28
S-5	0/2000	300

Seam Constant Load Test (SCLT)

Stress crack resistance should also be evaluated for the FML seams as well as for the sheet, since the seams are probably the most vulnerable parts of the entire liner system. The results published in a previous paper⁽⁴⁾ demonstrated that all types of HDPE seams can be vulnerable to stress cracking. Hence, a test method incorporating seams should be considered.

The proposed test, which is called a seam constant load test (SCLT) is very similar to the NCLT just described, except that a section of the seam is included in the test specimen. The constant neck section (120mm) must accommodate one edge of the seam where it joins to the parent sheet material. Note that there is no induced defect (i.e. there is no deliberate notch) in the specimen to initiate cracking. The discontinuities around the seam are the focus for crack initiation. Figure 5 illustrates the types of configurations to be used for the major types of HDPE liner seams.

Twenty test specimens, ten from each side of the seam on the upper and lower FMLs, are subjected to a load and then immersed in a 10% Igepal/90% tap water solution at 50°C. The applied load is recommended to be 45% of the yield stress of the sheet material at 50°C. The present duration of the test is 1000 hours. The specimens will respond in one of three ways; elastic, plastic, or cracked as described previously. Based upon past experience in testing of this nature, the following criteria should be considered for seams to avoid stress cracking vulnerability:



(a) Fillet Extrusion Seam

(b) Flat Extrusion Seam

(c) Hot Wedge Seam
Hot Air Seam
Ultrasonic Seam

Fig. 5 - Sketches of seamed test specimens in tension in a seam constant load test (SCLT)

- (a) No brittle failure should occur in any of the 20 test specimens within 24 hours
- (b) No more than five (5) brittle failures of the twenty test specimens should occur within 100 hours.
- (c) If less than five brittle failures occur within 100 hours, then the average of all brittle failures up to 1000 hours test duration should be greater than 300 hours.

Temperature Reduction of Exposed HDPE Geomembrane

In all three of the above described tests, elevated temperature is used to accelerate the crack growth rate. Chan and Williams⁽⁵⁾ indicated that crack growth rate is increased 40% for every degree Celsius rise in temperature. Since crack growth rate is directly related to brittle failure one can anticipate a similar proportionality. Therefore the surface temperature of the liner will probably have a direct effect on stress crack behavior.

The temperatures of exposed liners can be very high. A maximum temperature of 67°C (178°F) has been recorded on a black roof membrane in southern Florida⁽⁶⁾. If that is the surface temperature of an exposed FML, a particular crack will grow 1400% faster than one which is at 30°C temperature. In addition, ultraviolet degradation will be another action on the exposed FML which could have synergistic effects with the elevated temperature. Choi and Broutman⁽⁷⁾ found 90% reduction in the brittle failure time of HDPE after 250 hours of UV exposure using a UV fluorescent weatherometer. The minimization of one or both of these actions (temperature and ultraviolet light exposure), would definitely extend the performance of the FML.

Toward gaining insight into surface temperature moderation, a number of laboratory trials on exposed liner have been attempted. For these experiments a sheet of HDPE liner was fitted with a thermocouple directly on its surface and placed under a heat lamp. Three different trials were examined. They are as follows:

- soil covering
- sacrificial covering of liner
- light colored surfaces

Regarding soil covering experiments, various thickness of a well graded quartz sand were placed above the liner to note the changes in liner temperature with time. Figure 6 presents these results. Here it is seen that soil coverings of more than two (2) inches are required before meaningful temperature reductions accrue. More from a practical point of view, however, the thinnest layer one could place on an FML without danger of damaging it is approximately six (6) inches. Unfortunately, soil coverings on FML's are problematic in their long term stability. Instability comes from gravitational forces, seepage forces, precipitation induced erosion and wind induced erosion from the contained liquid. Thus, without continuous maintenance, soil covering of the liner is only a short-term solution at best and one which is undoubtedly very expensive.

Several attempts at providing a sacrificial covering of various geosynthetic materials over the primary liner have been attempted. The sacrificial covering that has been used is itself a liner with a separating air space provided by either a geotextile or a geonet. Figure 7 shows the results of these trials insofar as the temperature of the primary (or underlying) liner is concerned. Here it can be seen that the geotextiles with the highest mass per unit area (hence largest thickness) provide the greatest temperature reduction effect even beyond that of the geonet. However, such a system would be very expensive.

Utilizing references from the roofing industry, which is heavily involved in flat roof waterproofing using polymeric liners, it was found that surface temperatures are greatly reduced using white colored liner materials as opposed to black liners. To note such an effect on HDPE liners, experiments were performed using a black liner and then the same liner but now painted white. The results are provided in Figure 8 and are quite startling. The difference in temperature between the two trials is in excess of 25°C (77°F). According to the previously stated reductions in stress crack growth from elevated temperatures, this temperature reduction represents a 1000% increase in stress crack resistance.

Summary

Since stress cracking poses a concern with exposed FML's made from HDPE, methods for evaluating the phenomena are necessary. The current bent strip

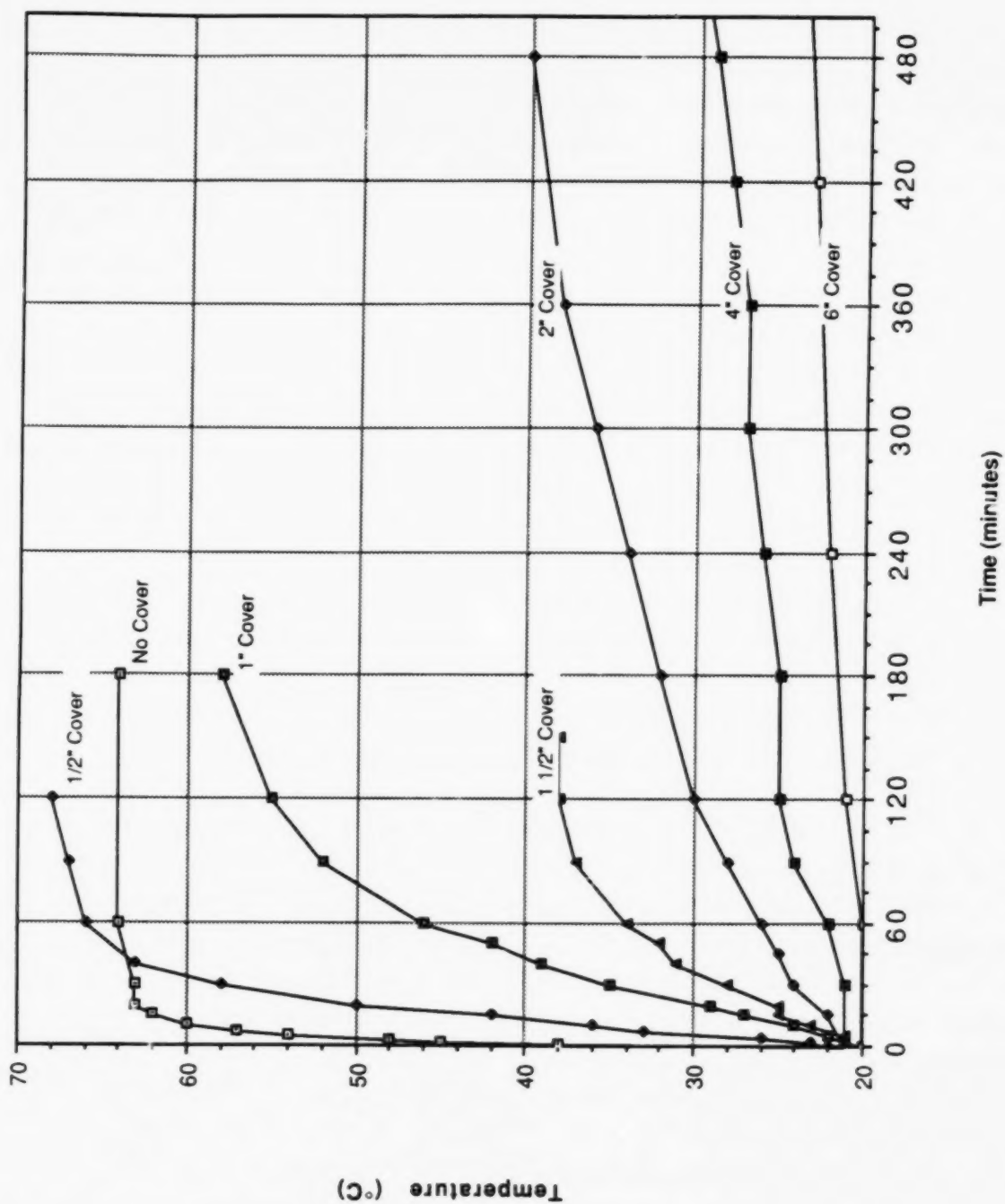


Fig. 6. - Surface Temperature Effects on a Soil Covered FML for Varying Soil Thicknesses

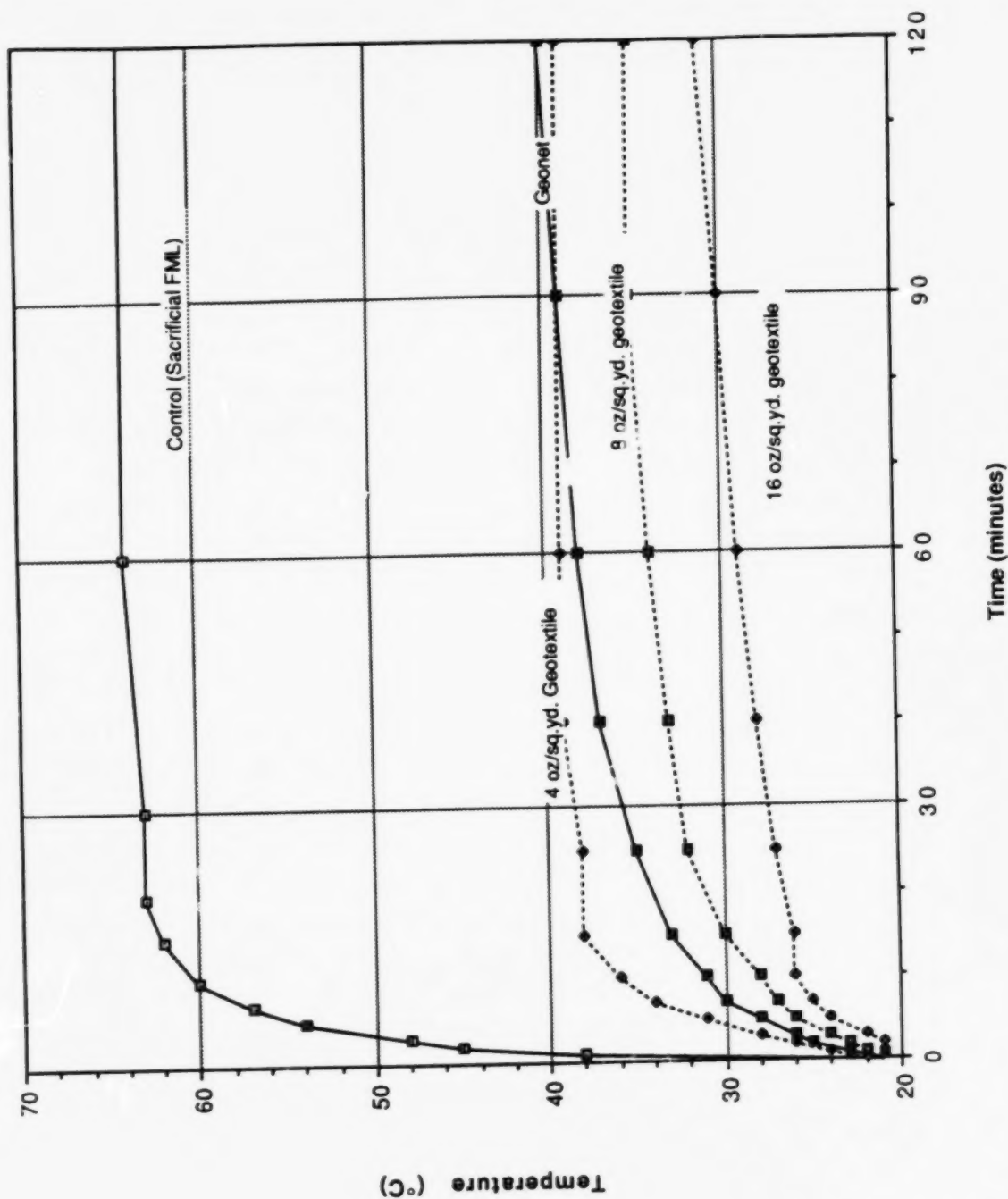


Fig. 7. - Surface Temperature Effects on Geosynthetic Covered FML for Varying Air Space Thicknesses Created by Geotextiles and Geonets

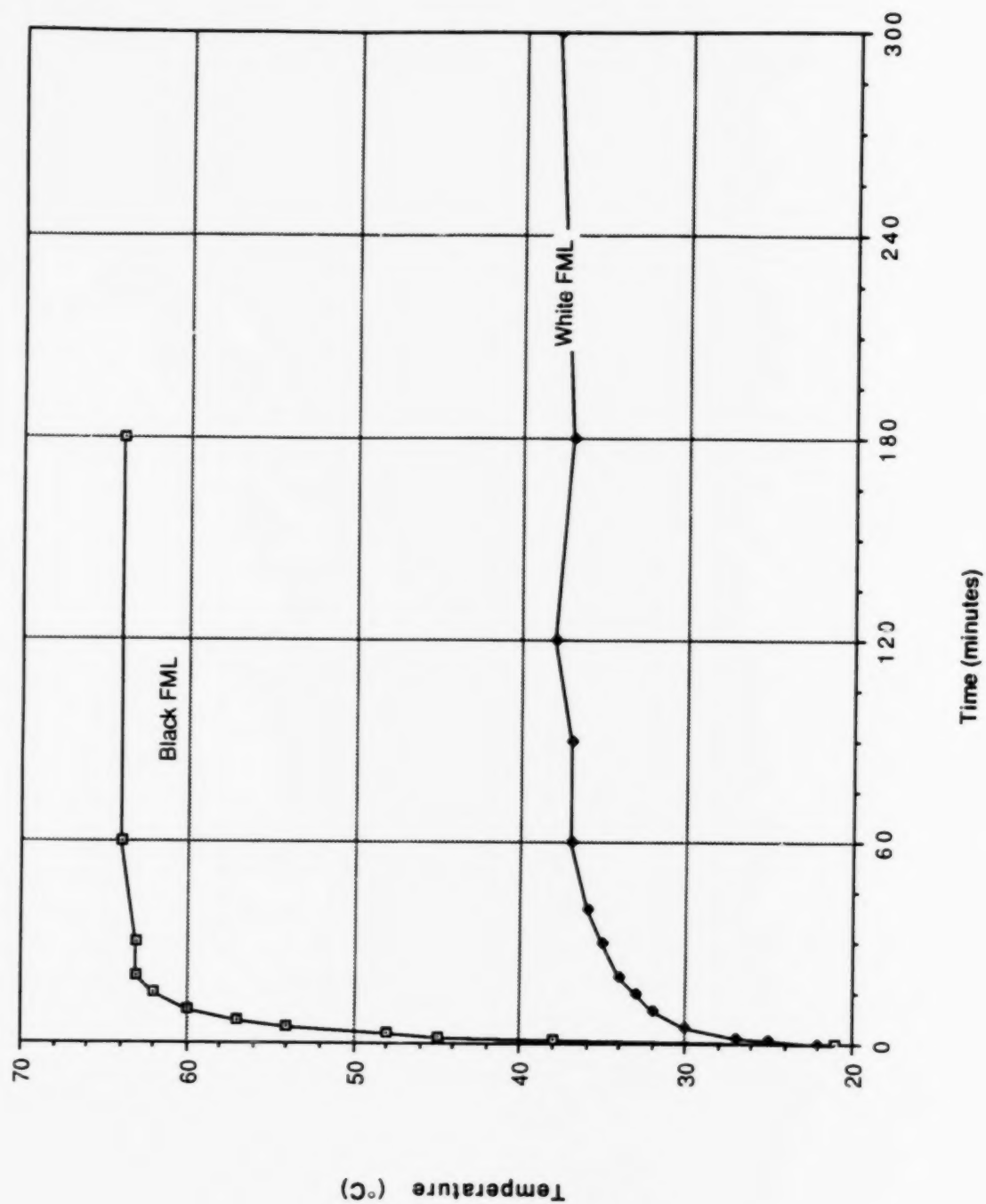


Fig. 8. - Surface Temperature Effects Between Black and White Surfaced FML's

test (ASTM D-1693) should be made more severe to better distinguish between different HDPE liners. An additional test for HDPE sheet materials, the notched constant load test (NCLT) does not allow for the stress relaxation of the polymer associated with the bent strip test. The NCLT determines the transition time between ductile and brittle failure modes. A minimum transition time for qualifying HDPE liners is currently being investigated. This same test setup can be used to estimate the stress cracking tendency of seamed samples. A test procedure called seam constant load test (SCLT) has been developed and has resulted in a set of criteria for evaluating an acceptable HDPE seam with respect to stress cracking potential.

Since the stress cracking potential greatly increases with a rise in liner temperature, a study was undertaken in this regard. The methods examined to minimize the liner's temperature included soil covering of varying thicknesses, a sacrificial liner separated by either geotextile or a geonet, and a white painted FML. Of these alternates the last one, i.e. the white colored FML, is very intriguing and should be explored further. It may well be that all exposed FMLs for longer than a specified time should be limited in their maximum surface temperature.

Acknowledgements

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LANDFILL TEST CELLS
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The Delaware Solid Waste Authority (DSWA) is a special Authority of the State of Delaware expressly created to manage the disposal of municipal solid waste generated in the State of Delaware. By the time the Authority was created in 1975,⁽¹⁾ only 7 active landfill sites were receiving waste, and 35 other sites were shut down because they failed to meet the state's new landfill regulations adopted in 1974. Those regulations imposed, as a minimum, the requirement of liners, leachate collection systems, gas vents and groundwater monitoring. Only one of the seven remaining sites, the Pigeon Point Landfill near Wilmington, Delaware, had a leachate collection system.

DSWA PROGRAM

DSWA initiated a program to construct new landfills in 1978. Its first new landfill was opened at Sandtown, Delaware on October 23, 1980. This was also the first landfill in the state to utilize a 30-mil. PVC flexible membrane liner (FML). In January 1981, DSWA acquired the operating responsibility for the Pigeon Point Landfill and subsequently made extensive improvements including an expanded groundwater monitoring program and a peripheral leachate collection system at the toe of the above-ground mound-type landfill. In September 1984, the Authority opened its Southern Solid Waste Facility at Jones Crossroads. This facility is another above-ground mound-type landfill; however, because of the high water table, this mound type landfill utilizes two 30-mil. PVC FMLs with the drainage layer between the two FMLs.

In October 1985, the Authority opened its third new landfill at Cherry Island. This facility is constructed on compacted silt dredged by the U.S. Army Corps of Engineers from the Delaware River and Port of Wilmington shipping channels. This facility is also an above-ground mound-type landfill, like the Cherry Island Landfill, with extensive leachate collection, gas venting and groundwater monitoring systems.

The Authority's three landfills serve the entire state's needs. In calendar year 1989, the three landfills received 707,000 tons of waste. Delaware is perhaps the only state with a policy of neither exporting nor importing solid waste.

⁽¹⁾ 7 Del. C. Chapter 64

LANDFILL OPERATIONS

The Central Solid Waste Facility was the first facility where we could measure leachate production from a new cell. The first 9-acre cell with a simple leachate collection line showed very low volumes of leachate production. Rather than pursuing leachate treatment and disposal options, the Authority decided to attempt recycling leachate through the cell, using Pohland's⁽²⁾ postulation that leachate recycling would be beneficial to maintain the organic materials degradation process in the landfills. Leachate recycling at this cell was reasonably successful and the concept was extended to the new cells at both the Central and Southern Solid Waste Facilities. Between October, 1980 and February, 1989, no leachate was removed for disposal. Therefore, the concept was deemed a success; however, there were some side effects. Periodically spray irrigation of leachate on the open face created odorous aerosols. It was not a reliable method because of the vagaries of weather conditions and was therefore abandoned. Leachate seeps started appearing on the side slopes. In order to prevent the leachate escaping outside the cell boundaries, major repair work was necessary. Most seeps appeared because (a) presence of plastic sheets or bags in the waste impeded the movement of leachate through the fill material, (b) compacted daily cover sometimes acted as a barrier when the daily cover had a high clay content, (c) short circuiting resulted when the movement of leachate was impeded (the path of least resistance is followed) and (d) the leachate mound started to build up.

The attempt to correct these problems resulted in complicating the water balance around the cells. It was difficult to use these cells to check the leachate production rate against the HELP⁽³⁾ model or the Mather-Thornthwaite⁽⁴⁾ water balance equations. In view of the impending avalanche of both state and federal regulations on solid waste disposal,

⁽²⁾ Pohland, F.G., Sanitary Landfill Stabilization with Leachate Recycle and Residual Treatment. EPA-600/2-75-043, October, 1975

⁽³⁾ Schroeder, P.R. et al. (1984a). "The hydrologic evaluation of landfill performance (HELP) model. "User's guide for version I, EPA/530-SW-84-009, 1, U.S. EPA, Ofc. of Solid Waste and Emergency Response, Washington, DC and Schroeder, P. R., Gibson, A.C. and Smolen, M.D. (1984b). "The hydrologic evaluation of landfill performance (HELP) model. "Documentation for Version I, EPA/530-SW-84-010, 2, U.S. EPA, Ofc. of Solid Waste and Emergency Response, Washington, DC

⁽⁴⁾ Thornthwaite, C.W. and J.R. Mather, 1957. Instruction and Tables for Computing Potential Evapotranspiration and the Water Balance. Publications in Climatology, Laboratory of Climatology 10(3).

DSWA thought it was prudent to test and quantify the benefits of leachate recycling. It was also important to find out the merits of operating landfills under moist conditions as opposed to maintaining dry conditions. Since external leachate treatment is quite expensive, leachate circulation helps reduce the cost of treatment. In fact, most newly adopted state regulations and the proposed Subtitle D Regulation of EPA require prompt removal of leachate and eventually drying up the landfill after the impervious capping system is installed.

TEST CELL PROGRAM

The Authority's objective was to observe the difference between "moist" and "dry cells". Although such studies have been attempted in laboratories and in small test plots, no controlled test in a "real" landfill environment had been attempted. Moisture is needed to support biological activity within the landfill. If a landfill cell is capped with an impermeable cover to prevent infiltration and the leachate is continuously withdrawn, it will gradually lose moisture and biological activity will slow down. Landfill gas production could be used as an empirical index of such activity. If it could be shown that "moist" landfill cells offer a better environment for continued biological degradation of the easily degradable organic fraction of the solid waste, as compared to dry landfills, the "post-closure" monitoring period of such cells could be reduced because the cell will have achieved stability.

Although a dry cell may appear to be stable, during the post-closure monitoring period any cracking of the cap could result in water infiltration. Such an event would gradually trigger biological activity again within the cell. If the cell is not carefully monitored, the increase in biological activity may not be noticed until it becomes a serious problem.

In this context, it is important to measure the difference. Therefore, the Authority decided to construct two landfill cells, each one acre in size. In Test Cell #1, provisions are made to recirculate the leachate while Test Cell #2 will be allowed to become dry. Each cell will receive household solid waste from the same select area and, therefore, contain similar materials. Initial estimate showed 11,000 tons capacity in each cell, compacted to the minimum 1,000 lbs. per cubic yard density used by the Authority. The same contractor operating the Authority's main landfill cell at its Central Solid Waste Facility operates the test cells also.

This program also offered an unusual opportunity to test other variables in the landfill design such as liners, leachate collection systems, etc.

CONSTRUCTION DETAILS

Site preparation was initiated in June, 1987. Each cell was designed to accommodate four different flexible membrane liners (FML) as primary liners. Figure 1 shows the details of the cells. The liner materials used are (1) 36-mil. CPE-R, (2) 36-mil. Hypalon CSPE-R, (3) 30-mil. PVC, and (4) 30 mil. CPE. A 30-mil. PVC liner was used as the secondary liner. Figure 2 shows details of settlement plates and instrumentation. Figure 3 shows the relative location of the test cells within the Authority's Central Solid Waste Facility. Figure 4 shows details in cross section. Figures 5 and 6 show the cross section of Test Cell 1 and 2 respectively. The primary and secondary liners are separated by a drainage layer which intercepts any leakage from the primary liners. Each cell has two leachate collection lines as shown in Figure 2. Each cell has its own drainage area. All the runoff from each drainage area is directed to a Parshall flume having a 12-inch throat width. Initially, an ultrasonic flow meter was used to measure the runoff. Because of its unreliability, a 90 degree V-notch was installed with the standard chart recorder to measure the runoff.

A standard weather station near the entrance to the landfill ($\frac{1}{2}$ mile away) provides information on humidity, wind speed and wind direction, solar radiation, temperature and precipitation. A special "acid rain" collector is also used to measure the acidity of the precipitation in central Delaware. A data logger is used to store and retrieve data. The construction cost of the cells was approximately \$800,000.

TEST CELL OPERATION

Actual filling started on August 1, 1989. Since the selected waste shed has garbage collection on Mondays through Fridays, the truck delivery pattern was adjusted to assure that both cells received waste collected on each weekday. Table 1 provides operating information for the first three months of the cell filling program.

CURRENT STATUS

The cells have reached almost 80% capacity. We anticipate closing out the test cells in May, 1990. By that time, each cell will have approximately 9,000 tons of waste. We have also attempted the use of foam as daily cover in both cells in lieu of soil to increase the volume of waste in the cells.

In September 1989 and February 1990, waste characterization tests were conducted. The information from those tests is shown in Table 2.

The U.S. EPA has provided a grant to study the chemical characteristics of the leachate. The Authority has contracted with Dr. F. Pohland of the University of Pittsburgh to conduct the chemical analysis and also assist in a review of the data from the program. Leachate samples are shipped to the University of Pittsburgh in special teflon bottles. Some tests such as pH, ORP (oxidation reduction potential), etc. are conducted in the field.

A series of time capsules in nylon netting, containing materials shown in Table 3 have been buried at select locations.

Each capsule and the materials in it have been tagged. It is proposed that one set of capsules will be exhumed approximately 2 years after the close of the cells, and the remaining capsules will be exhumed 5 years after the close of the cells.

Two sets of leachate samples have been sent to the University of Pittsburgh for analysis, and it is too early to report on any findings of the analysis. Data on precipitation, leachate production and runoff will be used to verify the HELP model predictions. Gas production will also be measured and gas samples will be analyzed for carbon dioxide, methane, oxygen, nitrogen and carbon monoxide.

This test cell set up affords an extraordinary opportunity to test other hypotheses on degradation of certain chemicals such as trichloroethene. The initial program will only compare the quality and quantity of leachate generated in each cell and the main cell (24 acres).

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

ACKNOWLEDGEMENT

The Authority gratefully acknowledges the grant assistance of U.S. EPA and the guidance given by Mr. R. Landreth and Mr. D. Carson.

TABLE 1. SUMMARY OF OPERATIONS

	August 1989		September 1989		October 1989	
	Test	Test	Test	Test	Test	Test
	Cell	Cell	Cell	Cell	Cell	Cell
	#1	#2	#1	#2	#1	#2
1. WASTE DELIVERED (Tons)	1269	1101	1059	1107	804	1000
2. OPERATING DAYS	12	11	10	10	10	10
3. TONS/DAY	106	100	106	111	124	148
4. PICK UP STOPS	48658	45677	50771	53121	40470	52595
5. LBS./STOP	52	48	42	42	40	38
6. VOLUME USED* (Cu. Yds.)	1773	1420	2226	2453	1878	2366
7. DENSITY (Lbs./Cu. Yd.)	1431	1551	1210	1141	1154	1085
8. COVER VOLUME (Cu. Yds.)	894	786	475	513	F	F
9. PRECIPITATION (Inches)	2.94	2.94	6.16	6.16	3.44	3.44

*Rusmar Foam - Is an aqueous based foam consisting of approximately 95% air, 4% water and 1% solids. The solids consist of surfactants and polymers which are completely biodegradable.

TABLE 2. COMPOSITION OF RESIDENTIAL WASTE

Category	September 1989 %	February 1990 %
PAPER		
Newsprint	13.88	12.79
Corrugated Cardboard/Kraft	7.89	6.71
Glossy Coated/Magazine	2.41	2.62
Mixed Paper	18.93	19.64
Total Paper	43.11	41.75
PLASTICS		
HDPE	0.62	0.59
PET	0.70	0.84
Films	4.21	3.28
Mixed Plastics	3.29	4.03
Total Plastics	8.83	8.73
GLASS		
Glass	3.58	4.97
Total Glass	3.58	4.97
METALS		
Aluminum (recyclable)	0.92	1.39
Ferrous	4.92	6.11
Other Non-Ferrous	0.03	0.04
Total Metal	5.86	7.53
ORGANICS		
Diapers	1.88	3.29
Textiles/Rubber/Leather	3.73	3.98
Yard Waste	10.71	4.74
Other Organics	21.02	21.16
Total Organics	37.35	33.17
INORGANICS		
Mixed Inorganics	1.13	2.58
Total Inorganics	1.13	2.58
HOUSEHOLD CHEMICALS		
Pesticides	0.00	0.01
Non-Pesticide Poisons	0.01	0.02
Paint/Solvent/Fuel	0.11	1.03
Automotive Products	0.02	0.03
Dry/Wet Cell Batteries	0.01	0.11
Miscellaneous Chemicals	0.00	0.06
Total Household Chemicals	0.16	1.27
OTHER		
Special Wastes (e.g. tires)	0.00	0.00

TABLE 3. MATERIALS INCLUDED IN TIME CAPSULES

1. CORN ON THE COB	44. NATIONAL GEOGRAPHIC
2. ORANGE	45. TIME/LIFE MAGAZINE
3. CHICKEN/BONES	46. LEAVES
4. STYROFOAM	47. TREE TRIMMINGS
5. MCDONALD'S STYROFOAM CONTAINERS	
6. WAXED PAPER CUPS	<u>CONSTRUCTION MATERIALS</u>
7. FRENCH FRY CONTAINERS	48. CPE
8. BIODEGRADABLE DIAPERS (UNUSED)	49. CPER
9. NON-BIODEGRADABLE DIAPERS (UNUSED)	50. PVC
10. DETERGENT BOXES (SMALL CONTAINERS)	51. HYPALON
11. DETERGENT BOTTLES (SMALL CONTAINERS)	52. PVC PIPE
12. UNBACKED CARPET	53. GEOGRID
13. RUBBER BACKED CARPET	54. GEOTEXTILES
14. NYLON	
15. ORLON	
16. COTTON	
17. PANTY HOSE	
18. HAIR SPRAY CANS	
19. NAIL POLISH	
20. SMALL PAINT CANS	
21. TRASH BAGS (UNIFORM MANUFACTURER)	
22. PLASTIC BREAD WRAPPERS WITH LABELS	
23. SCOTCH TAPE	
24. MASKING TAPE	
25. DUCT TAPE	
26. PHOTOGRAPHIC FILM	
27. PET BOTTLES (POLYETHYLENE TEREPHTHALATE)	
28. TFE DISKS (LOW DENSITY TEFLON DISKS)	
29. GARDEN HOSE	
30. PLYWOOD	
31. SOFTWOOD (PINE)	
32. IRON REBARS	
33. GALVANIZED PIPE	
34. LEAD-ACID BATTERIES	
35. HOUSEHOLD BATTERIES (D CELLS)	
36. CORRUGATED CARDBOARD	
37. WAX BACKED CARDBOARD	
38. REGULAR CARDBOARD (BINDER TYPE)	
39. DELAWARE STATE NEWS	
40. NEWS JOURNAL	
41. WALL STREET JOURNAL	
42. XEROX PAPER	
43. DSWA LETTERHEAD	

CENTRAL SOLID WASTE FACILITY TEST CELLS



LEGEND

- 4" LEACHATE SAMPLING WELL (Bottom Drainage Layer)
- 4" LEACHATE SAMPLING WELL (Solid Waste)
- ▲ 2" DRAINAGE LAYER PIEZOMETER

- ||||| PVC
- CPER
- CPE
- HYPALON
- GRAVEL

- PUMP STATION
- TANK
- 4" PERF. PVC
- 6" PERF. PVC
- SPRAY IRRIGATION CONNECTION BOX

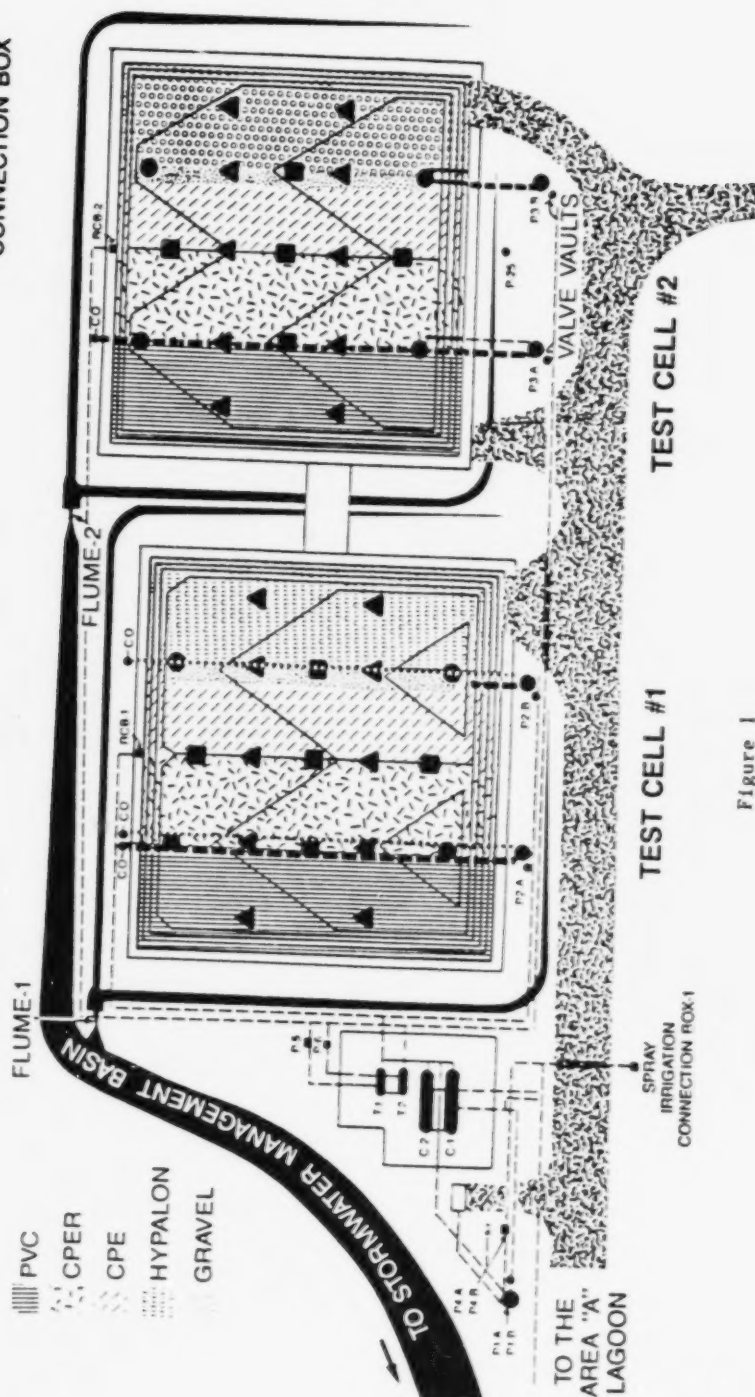
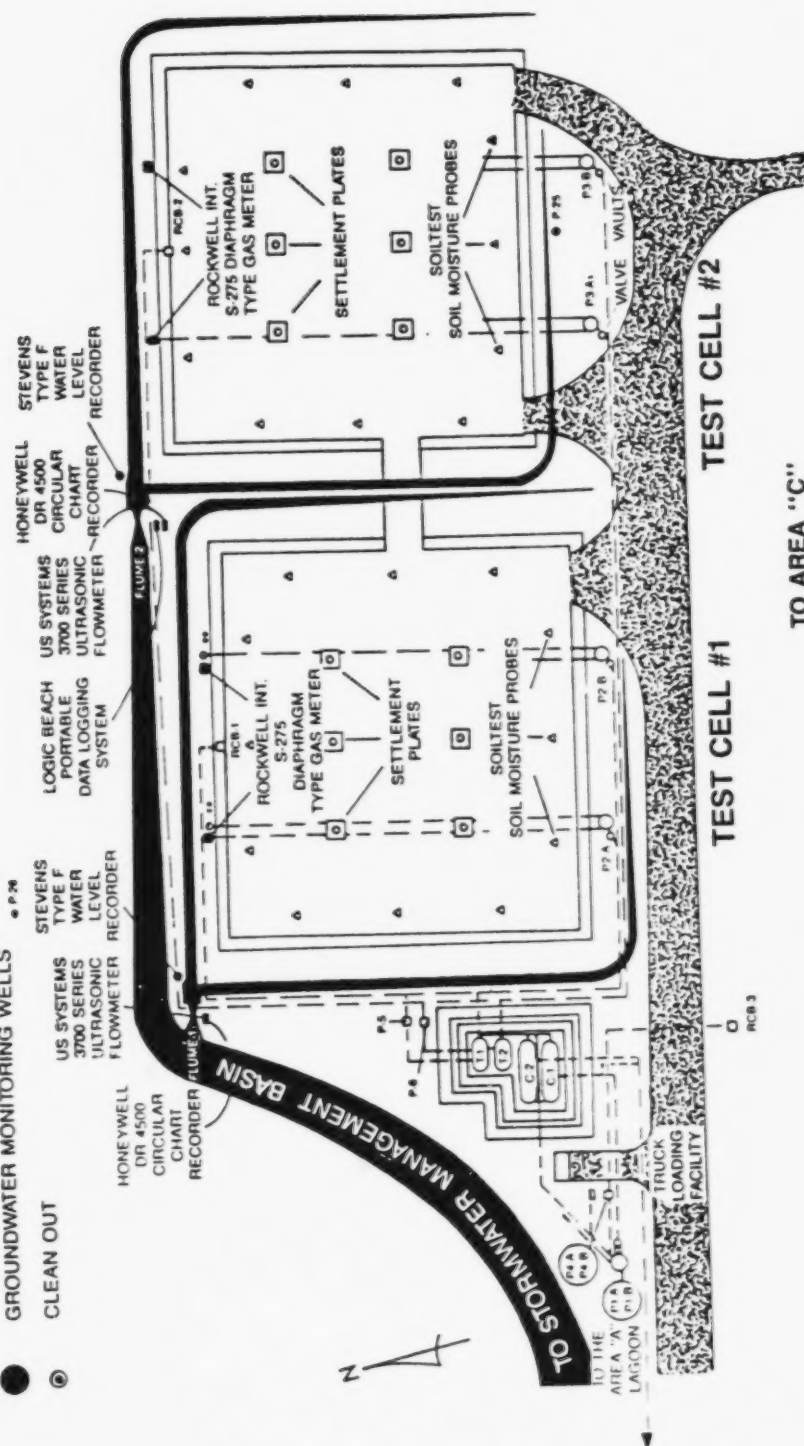


Figure 1

CENTRAL SOLID WASTE FACILITY TEST CELLS

LEGEND

- MAIN PUMP STATIONS
- LEACHATE STORAGE TANKS
- RECIRCULATION CONNECTION BOXES AND PUMPS
- GROUNDWATER MONITORING WELLS
- CLEAN OUT



TO AREA "C"

Figure 2

The diagram is a site map of the University of Maryland Environmental and Estuarine Science Laboratory. It shows three main areas: AREA A, AREA B, and AREA C. AREA A is located in the bottom left and contains SUMP A1 and SUMP A2. AREA B is in the middle and contains SUMP B1, SUMP B2, and SUMP B3. AREA C is in the top right and contains a row of monitoring holes labeled MH-1 through MH-10. To the left of AREA C is a STORMWATER MANAGEMENT BASIN with two test cells, TEST CELL 1 and TEST CELL 2, and two flumes, FLUME 1 and FLUME 2. A FIRE POND is located between AREA A and AREA B. The map also shows various roads, including a dashed line representing a road or boundary, and a hatched area representing a wetland or marsh. A north arrow is located in the upper left corner.

435

CENTRAL SOLID WASTE FACILITY TEST CELLS

TYPICAL CROSS SECTION OF LEACHATE AND GAS COLLECTION SYSTEMS

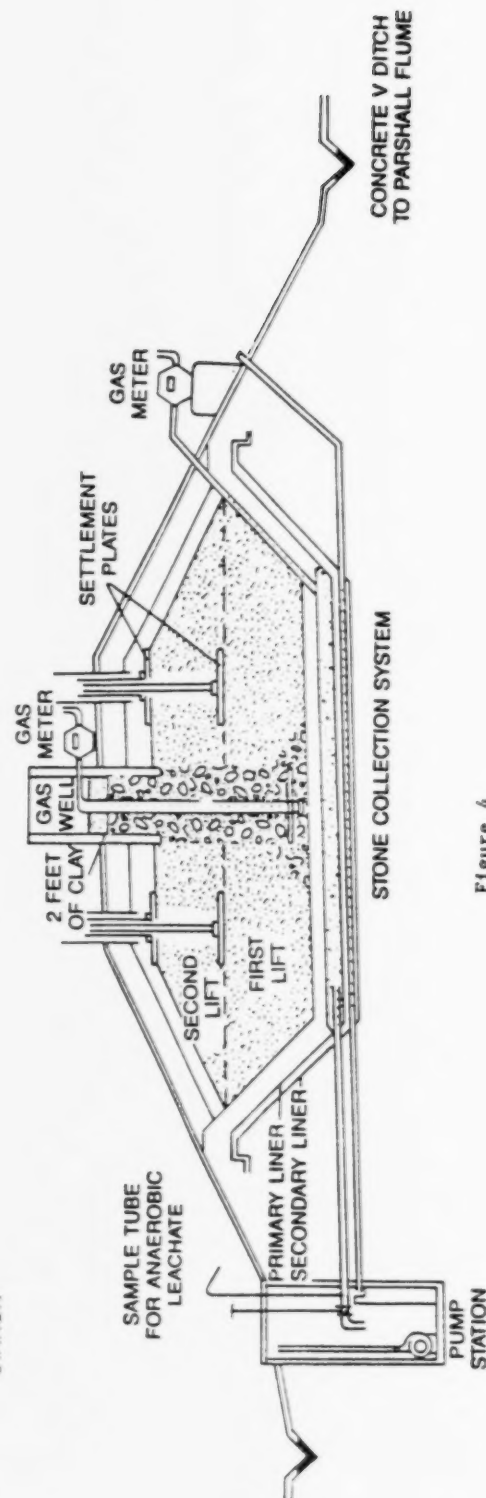
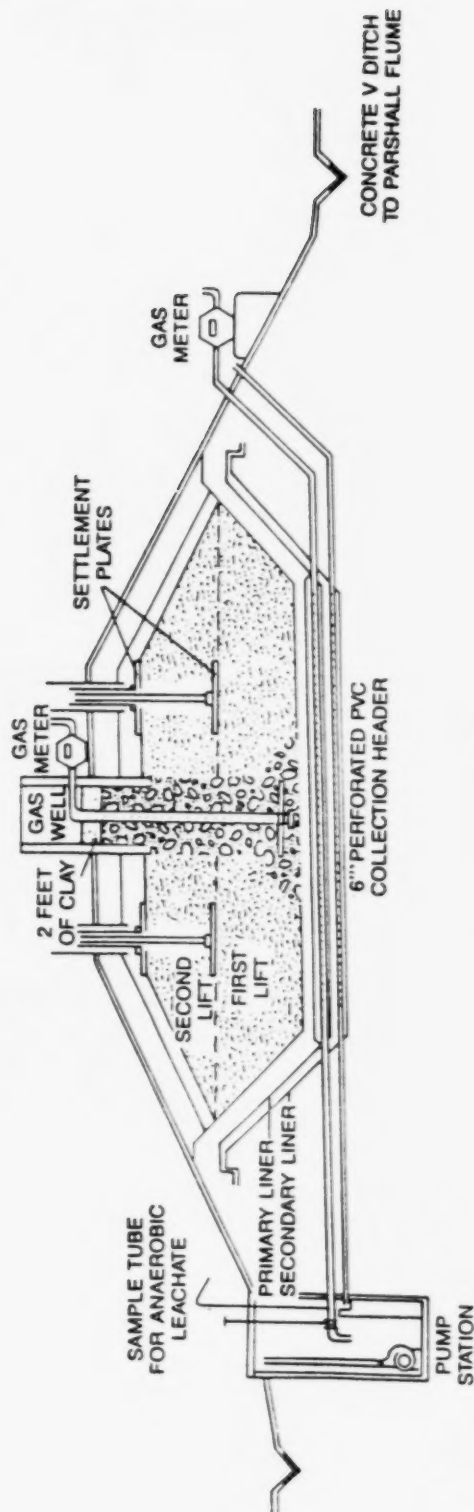


Figure 4



CENTRAL SOLID WASTE FACILITY

CROSS SECTION VIEW OF TEST CELL 1

LEGEND

- 4" LEACHATE SAMPLING WELL
(Bottom Drainage Layer)
- 4" LEACHATE SAMPLING WELL
(Solid Waste)
- ▲ 2" DRAINAGE LAYER
PIEZOMETER

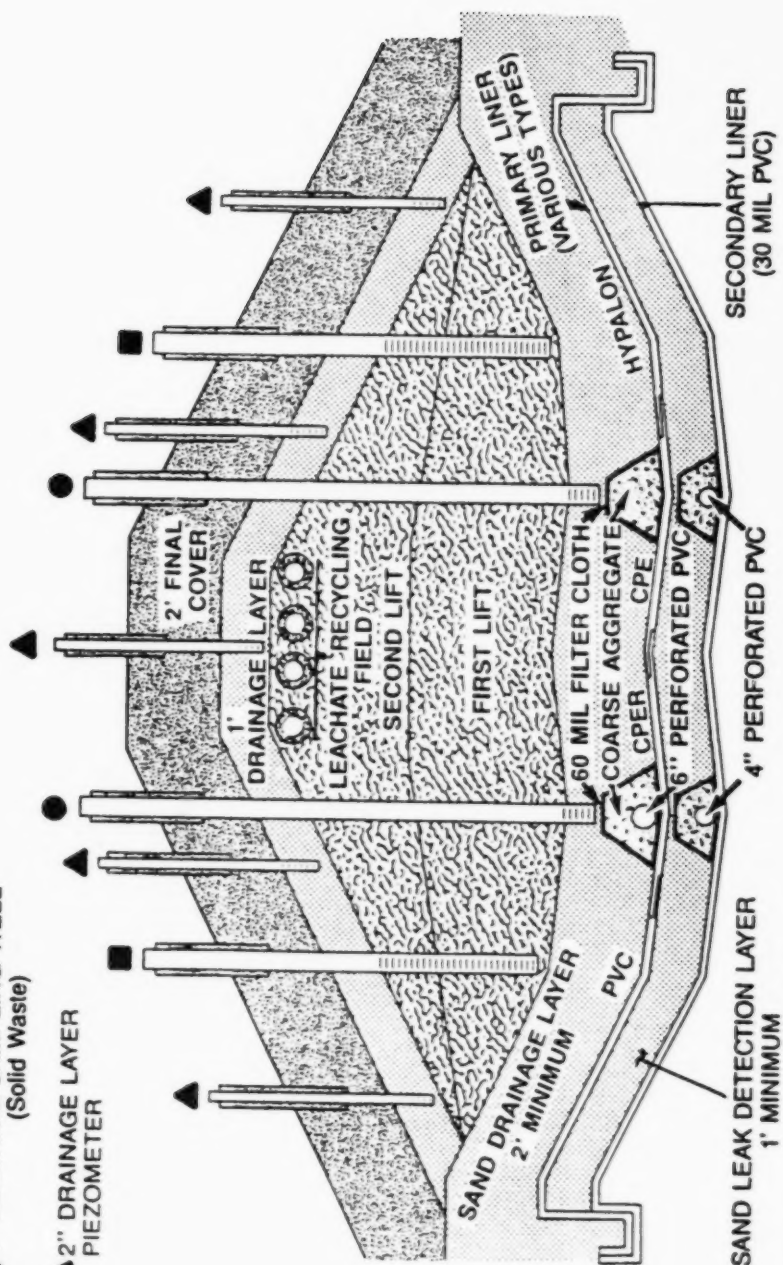


Figure 5



CENTRAL SOLID WASTE FACILITY

CROSS SECTION VIEW OF TEST CELL 2

LEGEND

- 4" LEACHATE SAMPLING WELL
(Bottom Drainage Layer)
- 4" LEACHATE SAMPLING WELL
(Solid Waste)
- ▲ 2" DRAINAGE LAYER
PIEZOMETER

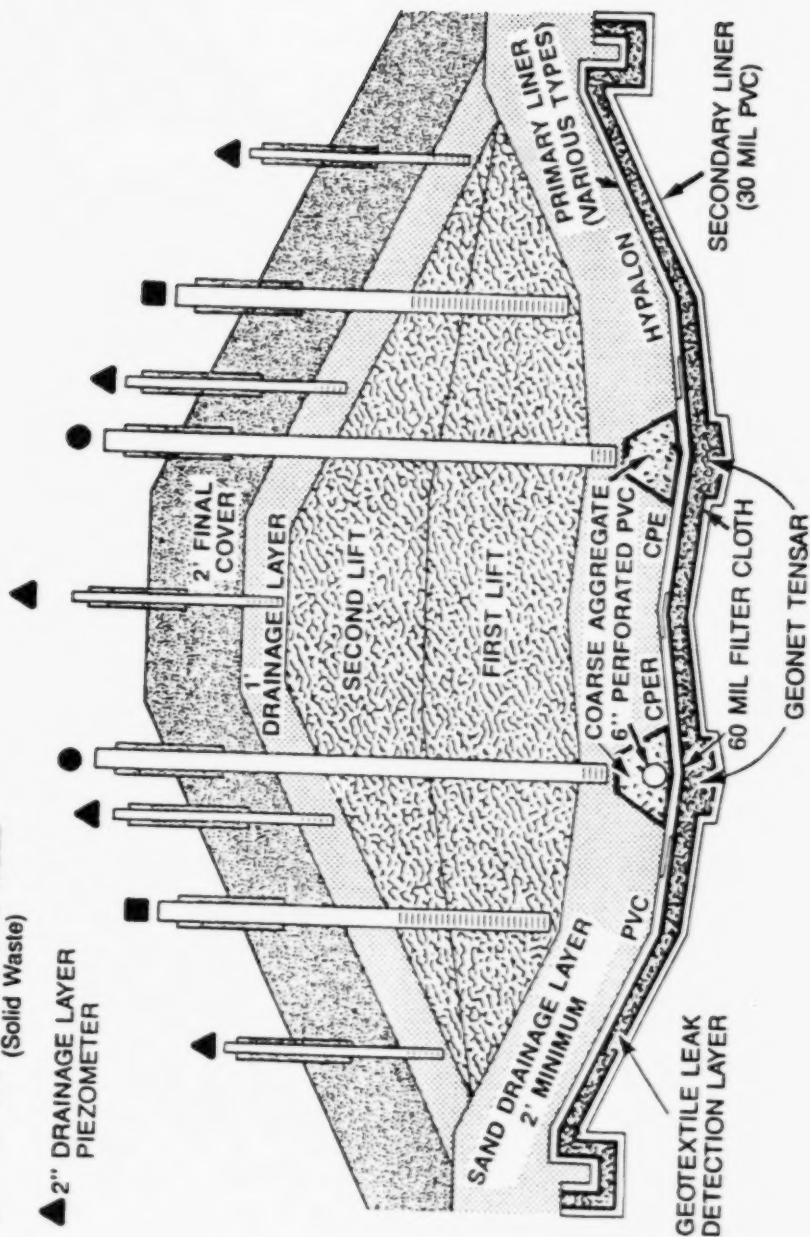


Figure 6

REVISION OF THE HELP MODEL

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ABSTRACT

The Hydrologic Evaluation of Landfill Performance (HELP) model was initially released in June 1984. Subsequently, two verification studies were performed, and the model has had widespread use and testing. The Hazardous and Solid Waste Amendments were enacted, and new minimum technology requirements were developed. Also, new technology has become available for use in landfills. These events have yielded numerous recommendations for revision of the HELP model. In response, drafts of Version 2 HELP have been developed, and its final draft is presently being completed.

The climatological data requirements have been changed to support a synthetic weather generator and a vegetative growth submodel added to the HELP model. The soil data input has been changed to allow specification of the initial moisture content of the various layers of material in the landfill profile. In addition, the default soil database has been updated.

Small revisions have been made to routines used to compute snowmelt, surface evaporation, plant transpiration and soil evaporation but the fundamental methods used are unchanged from the original version. The vertical drainage model has been updated to use a Brooks-Corey formulation for computing unsaturated hydraulic conductivity and vertical drainage. The lateral drainage model has been replaced with a new non-dimensionalized analytical solution of the Boussinesq equation. Additional submodels are now being prepared for inclusion in the final draft of this version. These include a method for determining the effect of surface slope of runoff, for estimating leakage through flexible membrane liners and for modeling lateral drainage from synthetic drainage nets. Other revisions have also been made, particularly in the output.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. The work described and presented herein,

unless otherwise noted, was developed from research conducted under sponsorship of the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency by the Environmental Laboratory of the U.S. Army Engineer Waterways Experiment Station. Permission was granted by the Chief of engineers to publish this information.

BACKGROUND

The Hydrologic Evaluation of Landfill Performance computer program (HELP) is a quasi-two-dimensional hydrologic model of daily water movement into, through and out of landfills. HELP accepts climatological, soil and design data and utilizes a variety of solution techniques to compute estimates of surface runoff, evapotranspiration, lateral drainage to collection systems, percolation through liners, average depths of saturation on the surface of liners and changes in soil moisture storage. Landfill systems composed of various combinations of vegetation, cover soils, waste cells, lateral drainage collection systems and relatively impermeable barrier soils, as well as synthetic drainage media and liners, can be modeled. The model is applicable to open, partially closed and fully closed sites, and facilitates rapid evaluation of a wide variety of landfill designs. HELP is a PC-based tool developed for use by both designers and regulators.

HELP is a water budget model that was developed to assist in design evaluations required by the Resources Conservation and Recovery Act (RCRA). Version 1 of HELP was initially released in June 1984 (Schroeder et al., 1984a; 1984b). Subsequently, two verification studies were performed, one comparing the field data from a total of 20 landfill cells from seven sites with HELP model results (Schroeder and Peyton, 1987a) and the other comparing experimental lateral drainage results from physical models with drainage estimates from the HELP lateral drainage submodel (Schroeder and Peyton, 1987b). The model was converted to run on IBM compatible personal computers in 1986, and since then more than 2000 copies have been distributed, generating extensive use and testing of model. In addition, since release of Version 1 of the HELP model, the Hazardous and Solid Waste Amendments were enacted and new minimum technology requirements were developed. Also, new technology has become available for use in landfills. These events have yielded numerous recommendations for revision of the HELP model. In response, drafts of Version 2 of HELP have been developed, and its final draft is presently being completed for release as Version 3. This paper presents the revisions of the HELP model.

MODEL DESCRIPTION AND REVISIONS

HELP was adapted from the Hydrologic Simulation Model for Estimating Percolation at Solid Waste Disposal Sites model of the U.S. Environmental Protection Agency (Perrier and Gibson, 1980; Schroeder and Gibson, 1982) and the Chemical Runoff and Erosion from Agricultural Management Systems (CREAMS) (Knisel, 1980) and Simulator for Water Resources in Rural Basins (SWRRB) models of the U.S. Department of Agriculture (USDA) Agricultural Research Service (ARS) (Williams et al., 1985). The following sections of

this paper present a description of all of the principal hydrologic and physical processes modeled by HELP and presents the revisions in each, including anticipated revisions to be included in Version 3.

INFILTRATION

Daily infiltration into the landfill is determined indirectly from a surface-water balance. Infiltration equals the sum of rainfall and snowmelt, minus the sum of runoff and surface evaporation. Runoff and surface evaporation are in part a function of interception. Precipitation on days having a mean temperature below 32 degrees Fahrenheit is treated as snowfall and is added to the surface snow storage. Decreases in snow storage occur by snowmelt and surface evaporation.

Precipitation

In Version 2 rainfall data may be synthetically generated in addition to the options of being specified by the user or selected from the default data base of historical rainfall data. The synthetic weather generator will be described later in this paper.

Snowmelt

Snowmelt is computed using a degree-day method with 32 degrees F as the base temperature (USDA, Soil Conservation Service, 1972); however, several small changes affecting the snowmelt have been made. The primary change is that Version 2 uses synthetically generated daily temperatures in the procedure instead of daily values interpolated from mean monthly temperatures. The inches/degree-day snowmelt constant was also increased from 0.06 to 0.10, a value more typical of open areas. Finally, Version 2 permits a small quantity of snowmelt to occur at mean daily temperatures between 23 and 32 degrees F to account for the variation in temperature during a day and for the fact that landfills often have higher soil temperatures due to heat generated from biodegradation.

Runoff

HELP models surface runoff using the Soil Conservation Service (SCS) curve number method, as presented in the Hydrology Section of the National Engineering Handbook (USDA, SCS, 1972). However, several small changes have been made in its application in Version 2. The relationship between the curve number for moderately wet conditions, antecedent moisture condition (AMC) II, and dry conditions, AMC I, has been revised to better cover the entire range of possible curve numbers. The soil moisture content which corresponds to AMC I, yielding the maximum storage retention parameter, has been increased to compensate for the larger evaporative zone depths used in Version 2. For the same reason the weighting factors for computing the effective soil moisture content used to determine the daily curve number or storage retention parameter have been changed to weight the near surface materials slightly less. Version 3 will include a procedure to adjust the curve number as a function of surface slope since surface slopes greater than 20 percent can produce significantly greater runoff.

Surface Evaporation

Surface evaporation is significantly reduced in Version 2. It is limited to the smaller of the potential evapotranspiration and the sum of the interception and the snow storage. Version 1 limited it to the smaller of the potential evapotranspiration and the sum of the snow storage and the quantity of the rainfall that did not contribute to runoff.

Interception

Interception was not modeled in Version 1. In Version 2 the interception approaches the maximum interception exponentially as the rainfall, RAIN, increases. The maximum interception is a function of the quantity of above ground biomass or leaf area index, LAI, and is limited to a maximum of 0.05 inches based on the work of Horton (1919). Interception, INT, is computed as follows:

$$INT = INT_{max} [1 - \exp(-RAIN / INT_{max})] \quad (1)$$

$$INT_{max} = 0.05 (LAI / 3) \quad (2)$$

where INT_{max} is the interception storage capacity of the vegetation. The total LAI, active and dormant, is computed by a vegetative growth model described later in this paper.

Potential Evapotranspiration

HELP uses a modified Penman method to compute potential evapotranspiration. This method, developed by Ritchie (1972), is also used in the CREAMS program (Knisel, 1980). Version 2 increases the albedo from 0.23 to 0.6 when the surface is covered with snow. It also uses synthetically generated daily temperature and solar radiation instead of daily values interpolated from mean monthly temperature and solar radiation as used in Version 1.

SUBSURFACE WATER ROUTING

Subsurface processes modeled in HELP include evaporation from soil, transpiration by plants, vertical unsaturated drainage, percolation through saturated liners, leakage through flexible membrane liners and lateral saturated drainage. In modeling these processes, the soil moisture of each layer of the landfill profile being modeled is computed by sequential analysis proceeding forward through time. The soil moisture controls the rate of subsurface water movement by each of the subsurface processes, but the rates of water movement by these subsurface processes yield the resulting soil moisture. Consequently, the soil moisture and rates of subsurface water routing are computed simultaneously in HELP by an iterative process; however, soil evaporation and plant transpiration are computed first.

Soil Evaporation

HELP uses Ritchie's method of evaporation from soil (1972) as applied in the CREAMS (Knisel, 1980) and SWRRB (Williams et al., 1985) models;

however, several differences exist in its application in the two HELP versions. Version 2 calculates an evaporation coefficient for stage 2 soil evaporation instead of reading the value from input. The potential soil evaporation or stage 1 soil evaporation may also differ because it is calculated using the potential evapotranspiration and vegetative cover (above ground biomass) which are computed with different data in Version 2. The vegetative cover in Version 1 is described in input but computed using a vegetative growth model in Version 2. The vegetative growth model will be described later in this paper.

Plant Transpiration

HELP models plant transpiration in the manner of the CREAMS and SWRRB models (Knisel, 1980; Williams et al., 1985) whereby the potential plant transpiration is a linear function of the potential evapotranspiration and the active leaf area index. Differences between the two versions include the differences in determining the potential evapotranspiration and the active leaf area index as well as differences in the selection of an evaporative zone depth and in the manner in which the program limits the plant transpiration for low soil moisture. Version 1 suggested conservative values for humid regions while Version 2 suggests typical values (unrestricted by poor capillarity of coarse-grained materials and not enhanced by exceptionally good capillarity such as that of compacted clay) based on level of vegetation and geographical area. Version 2 restricts the plant transpiration by limiting the maximum quantity of water that can be transpired from a segment of the evaporative zone on a given day as in the SWRRB model (Williams et al., 1985); Version 1 limited plant transpiration in the manner of Saxton et al. (1971), Sudar et al. (1981) and Shanholtz and Lillard (1970).

Unsaturated Vertical Drainage

HELP models unsaturated vertical drainage using a unit hydraulic pressure gradient approach (saturated Darcy's law) approach where drainage occurs at a rate equal to the unsaturated hydraulic conductivity. Under this approach vertical water routing is only downward except in the evaporative zone where water is removed upward by evapotranspiration. Again, several differences exist between its application in Versions 1 and 2. Version 1 assumed a linear relationship between soil moisture and unsaturated hydraulic conductivity where the hydraulic conductivity equaled zero at a soil moisture equaling the field capacity, and the hydraulic conductivity equaled the saturated value at a soil moisture equaling the porosity. In Version 2 the unsaturated hydraulic conductivity is computed by the Campbell equation using Brooks-Corey soil parameters to define the shape of this power function (Brooks and Corey, 1964; Campbell, 1974). This approach incorporates the moisture retention properties (capillarity) of the soil in the determination. Version 1 stopped drainage at soil moistures equaling the field capacity while Version 2 stops drainage at wilting point. Version 3 will consider soil matrix interactions in the selection of the moisture content where the drainage from one layer into another will cease. This addition will handle the situation where a fine-grained material at a higher water content will not drain into a coarse-grained material at a

lower water content since the soil suction of the fine-grained material is much greater than the coarse-grained material. In addition, Version 1 assumed free drainage down to the liner while Version 2 will not allow drainage from one layer at a rate greater than the rate that the layer before can accept. Hence, free drainage is not assumed in Version 2, allowing placement of a lower permeability non-liner layer below a layer of higher permeability.

Percolation through Liners

HELP assumes percolation (saturated vertical drainage) for all leakage through soil liners. Percolation is computed by Darcy's law using the saturated hydraulic conductivity of the liner material. The head loss gradient is equal to the average head above the base of the liner divided by the thickness of the liner.

Leakage through Flexible Membrane Liners

Leakage through flexible membrane liners (FML) is modeled as a reduction of the cross-sectional area of flow through the subsoil below the FML. The rate of flow through the leaking subsoil is computed as the percolation rate through a saturated soil liner. This method provides good results for composite liners but is not very good for just a FML. Therefore, Version 3 will include an improved leakage model for FML based on the work of Brown (1987) and Giroud et al. (1989a; 1989b; 1989c).

Saturated Lateral Drainage

Both versions model lateral drainage using a steady-state analytical approximation of the numerical solution of the Boussinesq equation (Darcy's law for saturated lateral flow through porous media coupled with the continuity equation). However, different analytical approximations are used based on different approaches in their development. Version 1 uses a linearized Boussinesq equation as developed by Skaggs (1983) that was corrected to use average depth of saturation in the formulation instead of depth of saturation at the crest of the drainage layer or the peak depth along the drain slope. Version 2 converts the Boussinesq equation into a nondimensional form and solves it for two analytical solutions at the extremes in non-dimensional average saturated depth. These two solutions are then fitted with the same value and slope in an approximation that covers the rest of the range of non-dimensional depths. The approximation matched the numerical steady-state solution of the Boussinesq equation within 1 percent of the predicted drainage rate. The solution is not linear; therefore, Version 2 uses a Newton-Raphson method to converge onto the solution of the nonlinear approximation. Average depth of saturation is used in the model since HELP is quasi-two dimensional, composed of two one-dimensional drainage models (one vertical and the other lateral) coupled at the interface between the liner and the lateral drainage layer.

VEGETATIVE GROWTH

Version 1 of the HELP model computed daily leaf area index of actively

transpiring biomass from interpolating a 10-point description from input of the LAI as a function of growing season. The vegetative cover during the dormant season was modeled as 60 percent of the maximum active LAI.

Version 2 of the HELP model accounts for seasonal variation in active and dormant above ground biomass and leaf area index through a general vegetative growth model. This model was extracted from the SWRRB model developed by the USDA ARS (Williams et al., 1985). The vegetative growth model computes daily values of biomass and leaf area index based on a maximum allowable value from input, daily temperature and solar radiation data, mean monthly temperatures and the beginning and ending dates of the growing season. The maximum value of leaf area index depends on the type of vegetation, soil fertility, climate and management factors. The program supplies typical values for selected covers; these range from 0 for bare ground to 5.0 for an excellent stand of grass. HELP maintains a data file containing mean monthly temperatures and beginning and ending dates of the growing season for 184 locations in the United States. Vegetative growth is a linear function of the available solar radiation during the first 75 percent of the growing season. Growth can be limited by temperatures below 50 degrees F and low soil moisture. Vegetative decay is modeled as exponential decay and is also a function of temperature and soil moisture. The decay process is modeled continuously, both during the active growing and dormant seasons.

SYNTHETIC WEATHER GENERATION

HELP incorporates a routine for generating synthetic daily values of precipitation, solar radiation and mean temperature. This routine is part of the WGEN computer program for weather generation developed by the USDA ARS (Richardson and Wright, 1984) based on a procedure described by Richardson (1981). The HELP user has the option of generating synthetic daily precipitation data rather than using default or manually entered historical data. Regardless of which precipitation input option is chosen, the program generates synthetic daily values of mean temperature and solar radiation. The generating routine is designed to preserve the dependence in time, the serial correlations and cross-correlation between variables and the seasonal characteristics in actual weather data at the specified location.

Precipitation

Daily precipitation is generated using a Markov chain model and a two parameter gamma distribution model. The first-order Markov chain model generates the occurrence of wet or dry days. In this model, the probability of rain on a given day is conditioned on the wet or dry status of the previous day. A wet day is defined as a day with 0.01 inch of rain or more. The model requires two transition probabilities: $P(W/W)$, the probability of a wet day today given yesterday was wet; and $P(W/D)$, the probability of today being wet given yesterday was dry. Monthly values of these probabilities are stored in a data file for 139 cities in the continental U.S.

A two-parameter gamma distribution function is used to generate the precipitation amount on wet days. The two-parameter gamma distribution

describes the distribution of daily rainfall amounts. Monthly values of the two parameters are also stored in a data file. The coefficients were obtained from the WCEN program documentation (Richardson and Wright, 1984). Normal mean monthly rainfalls are being added to the data file to improve the generation of daily rainfall in Version 3.

Temperature

WCEN generates daily values of mean temperature using a weakly stationary normal distribution function. It assumes that daily mean temperatures vary in annual harmonic cycle (hence, weakly stationary) with the actual values distributed normally about the daily position on the harmonic cycle. Nine temperature coefficients and normal mean monthly temperatures are used to describe the distribution: the mean of maximum temperatures on dry days, the mean of maximum temperatures on wet days, the mean of daily minimum temperatures, the amplitude of the harmonic cycle of daily maximum temperatures, the amplitude of the harmonic cycle of daily minimum temperatures, mean of coefficient of variation of daily maximum temperatures, mean of coefficient of variation of daily minimum temperatures, amplitude of coefficient of variation of daily maximum temperatures and amplitude of coefficient of variation of daily minimum temperatures. These coefficients are stored in a data file for 184 cities in the U.S. along with the normal mean monthly temperatures.

Solar Radiation

WCEN also generated daily values of solar radiation using a weakly stationary normal distribution function. It assumes that daily solar radiation values vary in annual harmonic cycle (hence, weakly stationary) with the actual values distributed normally about the daily position on the harmonic cycle. Three solar radiation coefficients and the station latitude are used to describe the distribution: the mean of solar radiation values on dry days, the mean of solar radiation values on wet days and the amplitude of the harmonic cycle of daily solar radiation values on dry days. These coefficients are also stored in a data file for 184 cities in the U.S. along with the station latitude.

SOIL CHARACTERISTICS

HELP makes use of many different soil characteristics. Three soil characteristics used throughout the program are porosity, field capacity and wilting point. Saturated hydraulic conductivity is used in computing vertical drainage, lateral drainage and liner percolation. The porosity used here is an effective value, defined as the volumetric water content at saturation (volume of water per unit bulk volume of material). Field capacity is defined conceptually as the water content that occurs after a prolonged period of gravity drainage. Wilting point is defined conceptually as the lowest water content that can be achieved by plant transpiration. Field capacity and wilting point are defined more precisely as the volumetric water contents at capillary pressures of 1/3 bar and 15 bars, respectively. These four parameters can be specified directly by the user or selected from a table of 18 default soil textures. The table of default soil textures and

their soil characteristics values were revised in Version 2 based on data compiled by Rawls et al. (1982). The default values are mean values for 5350 horizons of 1323 soils from 32 states.

Version 3 will also require the water content corresponding to the residual saturation as input for each material. In addition, the user will have the option of specifying the other Brooks-Corey parameters, pore size distribution index and the bubbling pressure, in lieu of the field capacity and the wilting point. The porosity will still be required.

Other soil characteristics are used for specific purposes. The soil evaporation calculation makes use of an evaporation coefficient. This coefficient indicates the ease with which water can be drawn upward through the soil by evaporation. Version 2 computes this value using Ritchie's relationship (1972) while Version 1 obtains it from input. The SCS runoff curve number based on both soil characteristics and vegetative cover is input that is optional when the soil characteristics are defined from the table of default soil textures.

SOIL MOISTURE INITIALIZATION

Version 1 initialized the soil moisture of all layers below the evaporative zone to equal the field capacity. All layers in the evaporative zone were initialized at the average of the field capacity and the wilting point. All liners were assumed to be saturated. The user had no option of initializing the water content of the layers.

Version 2 provides the user an option of initializing the water content of all layers except liners which are assumed to be saturated. If the user elects to allow the program to initialize the water content, the program will attempt to initialize the water content of the layers to their steady-state values.

CONCLUSIONS

Revisions have been made in the modeling of virtually every process described by the model and in the much of the input data. Many of the changes are minor in nature but others are very significant. The effects of these changes may be insignificant for some designs and for some climates but quite significant for others. Comparisons have been made between the two versions for a total of 20 cells located in Wisconsin, California and Kentucky and are currently available in draft form. The water budgets generated by the two versions for many of the cells were similar but several were different. In particular, Version 2 should improve evaluations in arid and semiarid regions and during the winter in the northern regions.

Version 2 also greatly expands the capabilities of the HELP model. It permits the use of one more liner and three more layers and allows the use of larger slopes and longer drainage lengths for lateral drainage. It also increases the range of saturated hydraulic conductivity that can be used in the model to include values for the largest drainage media or synthetic

drain nets and tightest clays. The program includes synthetic weather generation and modeling of vegetative growth to simplify data requirements. Version 3 will also adjust the runoff based on surface slope and provide better modeling of all designs employing flexible membrane liners.

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WASTE MINIMIZATION ASSESSMENTS AT SELECTED DOD FACILITIES

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ABSTRACT

The Waste Reduction Evaluations at Federal Sites (WREAFS) Program consists of a series of evaluations and demonstrations for pollution prevention and waste reduction conducted cooperatively by the Environmental Protection Agency (EPA) and other Federal agencies. The objectives of the WREAFS Program include: (1) performing waste minimization opportunity assessments, (2) demonstrating waste minimization techniques or technologies at Federal facilities, (3) conducting waste minimization workshops, and (4) enhancing waste minimization benefits within the Federal community.

This paper describes the WREAFS Program support of DOD activities in the pollution prevention area, and provides an overview of current projects being conducted at the Philadelphia Naval Shipyard, Fort Riley (Kansas) Army Forces Command, and the Naval Undersea Warfare Engineering Station in Keyport, Washington. Also described is a waste minimization research project with the Air Force. These DOD waste minimization opportunity assessments have identified waste minimization opportunities for a range of industrial and military operations including: metal cleaning, solvent degreasing, spray painting, vehicle and battery repair, ship bilge cleaning, and torpedo overhaul. The resultant waste minimization recommendations are source reduction methods including technology, process, and procedural changes and recycling methods, which focus on reuse or recycling.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The purposes of the WREAFS Program are to identify new technologies and techniques for reducing wastes from industrial processes used by federal agencies and to enhance the adoption of pollution prevention/waste minimization (WM) through technology transfer. New techniques and technologies for reducing waste generation are identified through WM opportunity assessments and are evaluated through joint research, development, and demonstration (RD&D) projects. The information and data from these projects are then provided to both the public and private sectors through various technology transfer mechanisms, including project reports, project summaries, conference presentations, and workshops.

The waste minimization opportunity assessments are conducted by an assessment team that is composed of personnel from EPA, staff from the Federal facility that is cooperating in the program, and EPA's contractors. The assessments follow the procedures described in the EPA report Waste Minimization Opportunity Assessment Manual. This manual provides a systematic planned procedure for identifying ways to reduce or eliminate waste. The development of this procedure was supported by the Risk Reduction Engineering Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio.

As a result of joint waste minimization opportunity assessments (WMOA's), RD&D projects are identified with recommendations for pollution prevention. The demonstration projects are conducted under inter-agency agreements with joint funding by EPA and the cooperating Federal agency. Waste minimization workshops and other technology transfer methods are being used to communicate the results of these projects to the Federal community and the private sector.

WREAFS PROGRAM PROCEDURES

The WREAFS Program procedures used for conducting the waste minimization assessments are closely related to the WM procedures presented in the Manual. Figure 1 describes the course followed by a typical WREAFS project. The assessments consist of four major phases:

- (1) Planning and Organization - organization and goal setting;
- (2) Assessment - careful review of a facility's operations and wastestreams and the identification and screening of potential options to minimize waste;
- (3) Feasibility Analysis - evaluation of the technical and economic feasibility of the options selected and subsequent ranking of options;
- (4) Implementation - procurement, installation, implementation, and evaluation.

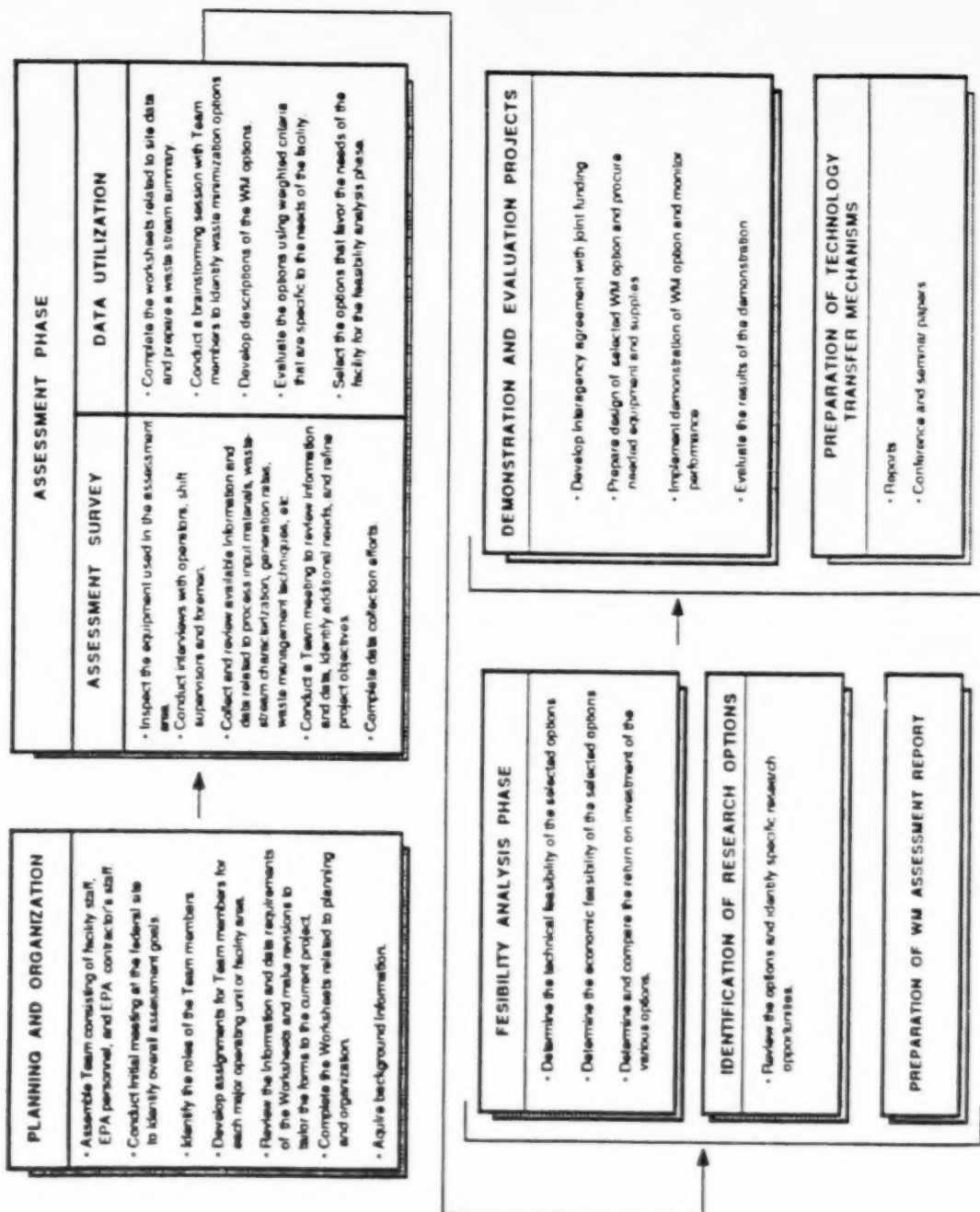


Figure 1. An Overview of the WREAFS Program

Many of the WM opportunities identified during WREAFS projects involve low-cost changes to equipment and procedures that may be presently employed at other Federal facilities or within private industry. These WM opportunities can often be implemented by the facility without extensive engineering evaluations. Some other WM opportunities identified during these projects will require further study before full implementation can be realized. Typically, opportunities requiring further evaluation are those that have the potential for affecting the process and/or require the use of new procedures or equipment. In such cases it may be necessary to conduct demonstration projects.

Demonstration and Evaluation Projects

The types of research projects that can be pursued under the WREAFS Program are those that are expected to advance the knowledge and practice of waste minimization technologies and methods, and have broad applicability to Federal facilities and private industry. Depending on the nature and state of development of the WM option selected for demonstration and evaluation, these projects may include: (1) process design, (2) detailed design and specification, (3) system procurement, (4) installation and start-up, (5) monitoring, and (6) reporting. Some projects may require bench-scale and/or pilot testing prior to or as a part of the demonstration project. Other projects may utilize full-scale equipment directly on the production line.

CURRENT PROJECTS

Four WREAFS projects are being performed at DOD facilities. These projects are in various stages of completion. The assessment survey has been completed for several projects and the waste minimization options and research opportunities have been identified. Other projects are just underway. The following is a description of each project.

PHILADELPHIA NAVAL SHIPYARD

This project is being conducted in cooperation with the Environment, Safety and Health Office of the Philadelphia Naval Shipyard (PNSY). The shipyard has an ongoing program for waste minimization. With their guidance, several industrial operations were selected for application of the new waste minimization procedures. The shipyard plans to utilize the results from this project as a guidance tool for evaluating waste minimization opportunities at other industrial activities at the PNSY. The results of this project will be particularly applicable to facilities that operate aqueous cleaning and spray painting processes. However, the procedures employed to identify and evaluate minimization alternatives are applicable to most industrial operations.

Facility Description

The Philadelphia Naval Shipyard is the nation's oldest continuously operating naval shipyard. The shipyard now specializes in revitalizing and

repairing ships already in fleet. The Service Life Extension Program (SLEP) is the shipyard's largest program. It is a comprehensive, keel-up restoration and modernization overhaul intended to extend the life of aircraft carriers by half, at about one third of the cost of a new carrier.

Selected Areas and the WM Options Evaluations

The procedure used for conducting the WM evaluation followed the EPA Waste Minimization Assessment Manual. The industrial activities selected for this project include areas used for the fabrication and surface coating of aluminum products, spray painting operations for steel parts, and a citric acid derusting operation, which is located at the drydocks.

The aluminum cleaning operation is performed to remove oil and other materials from the surfaces of aluminum sheets prior to welding. The cleaning line consists of four tanks: two process tanks, and two rinse tanks. The cleaning procedure consists of loading aluminum sheets into a metal basket, hoisting the basket into a process tank, and rinsing in one of the rinse tanks. The process water becomes diluted after repeated operation due to dragout losses and tap water replenishment. These tanks also collect floating oil, and the solution becomes contaminated with suspended solids. After approximately three months of operation, the process tanks are pumped to a tank truck and hauled by the contractor for disposal. The rinse tanks are operated as non-flowing rinses because of the low pH of the rinse water and the lack of facilities for neutralization. The rinse tanks are disposed of in the same manner as the process tanks but on a more frequent schedule, usually every two weeks.

Two WM options were evaluated for the aluminum cleaning operation. First, a dragout reduction and bath maintenance system was proposed. This system will include a hand-held spray rinse that will be applied over the process tanks. After affecting the parts, the rinse water will drip into the process tank. The spray rinse is expected to return 90 percent of the dragout back to the process tank. And 2, the acid baths accumulate oil and solids from the parts, and therefore, returning dragout losses may cause the process tanks to accumulate contaminants at a faster pace. These contaminants may interfere with the cleaning process; thus a bath maintenance system was recommended. This system would include an oil skimmer for floating oil removal and a cartridge filter for suspended solids removal. The dragout reduction and bath maintenance systems are expected to extend the usable life of the baths to one year.

A 2-stage rinse was proposed as an alternative to the existing rinse arrangement, where only one rinse tank is used after cleaning. The 2-stage rinse would make use of the existing tanks; however, some rearrangement was proposed to improve the layout of equipment and the efficiency of the operation. Using a 2-stage rinse would reduce the frequency of discarding the rinse water by allowing the first rinse to become more heavily contaminated. Then, after the first rinse is discarded and refilled with fresh water, the sequence of rinsing is changed (i.e., the cleanest rinse would always be the second rinse).

The spray painting processes are used for small and medium-sized aluminum parts, steel parts, and columns. Aluminum parts are degreased by wiping with rags that have been dipped into xylene. The parts are then spray painted in a water curtain booth. The painting process typically consists of a zinc chromate primer, air drying, a final enamel paint coating, and air drying. A new booth water chemical system was recently implemented. Spray painting of steel parts and columns is performed at various locations.

Several WM options were evaluated for the two spray painting operations. First, an operator training and awareness program option was evaluated that could reduce the amount of waste paint by controlling the amount of paint overspray, the amount of unused paint left in the can, and the amount of paint that is unusable due to partial solidification prior to use. Second, equipment changes were evaluated for the current compressed air paint spraying systems. Under consideration is the high-volume, low-pressure (HVLP) method. The transfer efficiency of HVLP is reportedly in the range of 65 to 90 percent. Compressed air equipment typically provides a 40 percent or lower transfer efficiency. Other WM options evaluated during the assessment included expanding use of a new paint booth chemical system and use of sludge dewatering equipment that would reduce the volume of paint sludge and recycle booth water.

PNSY employs a chemical cleaning process for ships' tanks, bilges, and void spaces termed the citric acid process. It is generally performed while ships are in drydock. This process is relatively new and it replaces the mechanical methods of cleaning and derusting metal surfaces. The process generates a spent citric acid/triethanolamine (TEA) solution. Owing to the significant material input costs and the high disposal costs, a recovery option was considered during the project.

Results at PNSY

The results of the assessment, which are presented in Table 1, indicated that the best options in terms of cost savings are the awareness and training program for paint waste reduction and the changes to the aluminum cleaning line including dragout reduction, bath maintenance, and improved rinsing. These three options offer a combined net savings in operating costs of \$158,680 per year.

The citric acid/TEA recovery option was identified as a potential research project. A preliminary process design was prepared for the recovery process that included an electrodialytic membrane unit for separation and removal of dissolved metals. This type of technology has been applied to similar chemical solutions; however, its application to this waste has not been previously demonstrated.

FORT RILEY, KANSAS

Fort Riley is a permanent U.S. Army Forces Command (FORSCOM) installation that provides support and training facilities for the 1st Infantry Division (Mechanized), Non-Divisional Units, and tenant

TABLE 1. PHILADELPHIA NAVAL SHIPYARD SUMMARY
OF WM FEASIBILITY ANALYSIS PHASE

Location Process & Waste	WM Options	Nature of WM Option	Total Cap. Investment \$	Net Op. Cost Savings \$/yr	Payback Period yr	Projected Waste Reduction lb/yr
<u>Building 990</u>						
Aluminum Cleaning Spent KRC-7X	Bath Maintenance Two Stage Rinse	Equipment Equipment	\$12,200 3,116	\$44,190 34,590	0.3 0.1	\$ 44,035 190,590
Spray Painting of Aluminum Paint Sludge	Booth Chemicals	Materials	12,190	5,430	2.3	-
	Paint Sludge Dewat.	Equipment	9,550	3,840	2.5	15,012
Used Paint Thinner	Awareness & Train.	Personnel/ proced.	24,266	79,900	0.3	unknown
Unused Paint	Awareness & Train.	Personnel/ proced.	See used paint thinner	-	-	-
<u>Building 1028</u>						
Spray Painting of Steel Paint Sludge	Booth Chemicals	Materials	3,300	5,460	0.6	27,022
	Paint Sludge Dewat.	Equipment	see bldg 990	-	-	-
<u>Drydocks</u>						
Citric Acid Derusting Conc. Citric Acid/TEA	ED Recovery System	Equipment	76,050	60,720	1.3	124,241

activities. It is a U.S. Government-owned, U.S. Government-operated facility. Fort Riley provides the U.S. Army with the capability to house and train an Army division and associated land combat forces as well as to service Army functions in an assigned Midwest support area.

Selected Areas and the WM Options Evaluated

The areas selected for assessment at Fort Riley were the Division motor pools located in various areas on the post. Routine mechanical maintenance is performed in these areas for trucks, tanks, armored personnel carriers, and other vehicles. Results of the Fort Riley, Kansas waste minimization assessment identified two waste reduction opportunities in a multipurpose building used for automotive subassembly rebuilding, lead acid battery repair, and other Army maintenance operations.

Battery acid (32-37 percent sulfuric acid) containing trace concentrations of lead and cadmium is currently drained from both dead batteries and batteries requiring repairs, e.g., replacement of battery terminals, and shipped in 15-gallon drums to a hazardous storage facility at the installation for ultimate disposal as a hazardous waste. It is proposed instead that the waste acid be gathered in a holding tank, filtered to remove any particulates, and adjusted in concentration to 37 percent sulfuric acid (using 60° Baume commercial sulfuric acid) as needed for reuse in reconditioned or new batteries. The buildup of dissolved metal impurities in this recycling system is prevented by purging part of the acid from the system. It is assumed in this assessment that 25 percent of the acid is purged and 75 percent is reused.

The dirty aqueous alkaline detergent solution for automotive parts cleaning, which contains trace concentrations of lead, chromium, and cadmium at a pH >12 as well as the oils, grease, and dirt removed from the automotive parts, is currently drained to an on-site nonhazardous waste evaporation pond. This waste, heretofore regarded as nonhazardous waste, is currently being reclassified as a RCRA hazardous waste due to its characteristics (D002, D006, D007, D008) and will have to be disposed of as a hazardous waste. The proposed waste minimization option for this waste stream involves emulsion breaking to remove the tramp oils, filtration to remove particulates, and addition of fresh alkaline detergent as necessary, followed by reuse for automotive parts cleaning. The buildup of impurities would be prevented by purging 25 percent of the used alkaline detergent and recycling 75 percent.

Results at Fort Riley

The waste reduction options identified in this study are recycle/reuse options. Presented in Table 2 are the results of the cost analysis phase. A net savings in operating costs is anticipated to be \$149,400 per year. The expected payback periods for the two waste reduction options identified are very short. Successful application of these options at Fort Riley would create the potential for similar waste minimization options in at least 10 other U.S. Army FORSCOM installations.

TABLE 2. SUMMARY OF WASTE MINIMIZATION OPTIONS COST ANALYSIS DATA AT FORT RILEY, KANSAS

Operation Waste Stream	Waste Minimization Options	Total Capital Invest. \$	Net Operating Cost Savings, \$	Payback Period, yr	Projected Waste Reduction lb/yr
Battery Repair Shop/Waste Battery Acid	Recycle of waste battery acid	15,200	37,400	0.41	51,291
Automotive Subassembly Rebuild/Tornado Parts Washer Wastewater	Recycle of Tornado washer wastewater	19,800	112,000	0.18	181,395

NAVAL UNDERSEA WARFARE ENGINEERING STATION, KEYPORT, WASHINGTON

This project is being conducted in cooperation with the Naval Energy and Environmental Support Activity (NEESA) of Port Hueneme, California, in coordination with the Environmental Protection Division (Code 075) of the Naval Undersea Warfare Engineering Station (NUWES) Staff Civil Engineering Department. Several departments at NUWES Keyport are involved in an ongoing program to further the process of waste minimization on the Station. The draft version of this waste minimization assessment is currently under review by the Naval Undersea Warfare Station and detailed results of the study are not available.

NUWES Keyport is located within the central Puget Sound area of Northwestern Washington State. In 1978, the facility changed names from Naval Torpedo Station Keyport to NUWES Keyport recognizing that the functions of the Station had broadened to include various undersea warfare weapons and systems engineering and development activities. The principal activities currently conducted at NUWES Keyport are the design and testing of torpedoes.

Selected Areas and the WM Options Evaluated

Potential sources for waste materials include torpedo as well as other ordnance handling and related activities. Specific activities on the Station include welding, plating, machining, and sheet metal work; painting and stripping; electrical work; carpentry; fuel storage and use; power production; pest control; sanitary and industrial wastewater treatment; and associated storm sewer runoff. These activities generate a variety of potentially hazardous wastes, including fuel, oil, coolant, hydraulic

fluid, and grease; various metals and plating bath liquids; paint and thinner; Freon, alcohol, mineral spirits, and other solvents; resin; acids and caustics; chromate and cyanide salts; wastewater treatment sludge; and detergent.

Two areas at the Station were examined in detail during the assessment. Both areas are used for the maintenance of torpedoes and have similar operations, processes, and waste streams. The major waste generating activities consist of defueling, disassembling, cleaning, reassembling, and refueling of torpedoes. The waste materials at these areas include: solids, liquids, sludges, solvents, and oils that are contaminated with Otto fuel, as well as diethylene glycol (DEG), mineral spirits (Agitene), and cyanide compounds. Waste minimization options were recommended for contaminated solids, contaminated liquids, and waste mineral spirits.

The waste minimization option for contaminated solids addresses all clothing that becomes soiled with Otto fuel (OF). Recommendations for the reduction of this waste are to segregate contaminated from non-contaminated clothing, and only dispose of the contaminated portion of a garment.

Automated parts cleaning is another waste minimization option recommended to reduce soiled clothing. In addition, the increased efficiency of an automated system will serve to reduce the amount of waste mineral spirits.

Contaminated liquids can be reduced in the Otto fuel tank draining area by installing another automated system that increases efficiency and decreases spills and contaminated solids.

At one site location, waste mineral spirits are currently pumped on a regular schedule from deep sink parts cleaners. This schedule is followed whether or not the solvents have become fouled. By monitoring the solvents and disposing only when fouled, the amount of waste cleaner will be reduced.

Preliminary Results at Keyport, Washington

The waste minimization options under consideration for NUWES Keyport are being evaluated for technical and economic feasibility. Projected waste reductions and costs are not available at this time.

U.S. AIR FORCE

In support of the Department of Defense's waste minimization program, the Air Force is seeking to obtain information for its chlorinated solvents recycling program. Air Force facilities are high-volume consumers of industrial solvents. Applications for solvents range from degreasing aircraft parts and missile guidance systems to cleaning small bearings and armament material. The major chlorinated degreasing solvent currently used by the Air Force is 1,1,1-trichloroethane. Due to toxicity and inherent health effects, the use of all chlorinated solvents may be curtailed unless

effective waste reduction and recycling programs are developed. In this effort, an assessment will be performed for the recycling program at a selected Air Force base. The project is being performed in cooperation with Auburn University. Objectives for the study include developing mitigation technology for minimizing the accumulation of toxic contaminants in the recycled product and addressing concerns regarding solvent inhibitors and additives. The results of the study will be used to formulate a model program and establish protocols for operating solvent recycling technology service programs.

SUMMARY AND CONCLUSIONS

Waste minimization opportunity assessments conducted under EPA's WREAFS program are an excellent mechanism for promoting pollution prevention research at DOD facilities. At the three DOD sites audited, waste minimization opportunities have been identified for the following hazardous waste streams: aluminum cleaning solutions, paint sludge, paint thinner, unused paint, citric acid derusting solutions, waste battery acid, parts washer wastewaters, contaminated clothing, parts cleaning solutions, waste Otto fuel, and waste mineral spirits.

Pollution prevention recommendations have been made for the Philadelphia Naval Shipyard and Fort Riley that will reduce hazardous waste generation by a minimum of more than 630,000 pounds per year, with an annual savings of \$383,530 at the two sites. In addition, a number of these opportunities will make excellent demonstration and evaluation projects.

The WREAFS program can be used as a catalyst to implement pollution prevention strategies and to identify research opportunities that would not be otherwise identified. Through this program EPA can assist DOD in transmitting new technical information to all of its facilities through project reports, workshops, seminars, and conferences.

CHEMICAL SUBSTITUTION FOR 1,1,1-TRICHLOROETHANE AND METHANOL
IN MANUFACTURING OPERATIONS

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ABSTRACT

Hazardous wastes are generated from cold solvent degreasing operations used in many industrial processes. The spent solvents are managed under Subtitle C of the Resource Conservation and Recovery Act (RCRA). With the land ban of spent solvents, disposal has become increasingly difficult. As a result, industries began investigating ways to avoid using RCRA-listed cleaning solvents. EPA's Pollution Prevention Research Branch along with APS Materials, Inc., a small metal finishing company, participated in a joint research project to evaluate the substitution of a dilute, terpene-based cleaner for 1,1,1-trichloroethane (TCA) and methanol, hazardous wastes F001 and F003 respectively, in their degreasing operations.

This paper presents the results of a study evaluating the waste reduction/pollution prevention that can be achieved by substituting dilute limonene solutions for TCA and methanol in the cleaning of orthopedic implants (e.g. metal knee and hip replacements). This paper describes the original cleaning process, the modifications made to the process in using the dilute limonene solution, and the sampling plan used in evaluating the effectiveness of the solution. The paper presents qualitative results of the sampling tests and an economic evaluation of plant modifications.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Passage of the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) of 1976 has redirected the U.S. environmental policy towards waste minimization to improve the quality of the environment. In its efforts to pursue the objectives set forth by Congress in the HSWA to RCRA, the USEPA has established a national comprehensive pollution prevention program that includes information gathering, research and development, demonstration, support of state and local government pollution prevention programs, training and education, technology transfer activities, pollution prevention assessments, and extensive communications with universities and the general public. Implementation of programs to achieve several of these objectives is accomplished through research conducted by the Pollution Prevention Research Branch of the Risk Reduction Engineering Laboratory. This research addresses the intent of the Amendments to reduce the release and transport of hazardous, toxic, and nonhazardous materials through the air, water and solid media. The research is of significant benefit to the USEPA, states, waste generators, and the general public since results of this research will assist in reducing the generation of pollutants that threaten both public health and the environment. The principal goal of the Pollution Prevention Research Branch is to encourage the identification, development, and demonstration of processes and techniques that result in less waste being generated in order to promote a more rapid introduction of effective pollution prevention techniques into broad commercial practice.

1,1,1-trichloroethane (TCA) is used as a cold solvent degreasing agent in many industrial degreasing processes. In 1986, TCA was identified as a hazardous waste that must be managed under Subtitle C of the Resource Conservation and Recovery Act. As a result of this action, industries began looking for ways to avoid the use of TCA cleaning solvents. The EPA decided to target the metal finishing industry for participation in a joint research project to examine the possibility of substituting a terpene-based cleaner for TCA in degreasing operations. APS Materials, Inc., a facility in Dayton, Ohio participated in the research project. APS Materials, Inc. is a metal parts finishing company which generates TCA and methanol waste from cold solvent degreasing operations associated with their plasma spray deposition process.

PLASMA SPRAY DEPOSITION PROCESS

The plasma spray deposition process has emerged as a major means to apply a wide range of materials on diverse substrates. The deposition process is accomplished with the use of a plasma gun. In the plasma gun, an electric arc is formed between positive and negative electrodes via an electric discharge initiated by direct current. The discharge gives rise to a breakdown of the dielectric nature of the gas, making it conductive. The net result is a gaseous collection of energetic electrons and ionized molecules known as a plasma. The plasma exits as a high velocity flame through the nozzle of the gun. A powdered feedstock is injected into the flame via a carrier gas (usually argon). The injected powder accelerates, melts, and is carried at sonic velocities to the substrate on which the particles impact and solidify rapidly, at rates about one million degrees per second, building a well adhered protective coating.(1)

While APS Materials, Inc. employs the fundamental plasma spray deposition process, a few changes were made to better accommodate the plasma spray work performed by their company. First, APS Materials performs its plasma spraying in an inert atmosphere chamber. This is done for cooling and to prevent the titanium powder used in many of its coating applications from becoming oxidized thus forming brittle coatings. APS Materials also uses helium in the spray gun as a mix gas and to adjust the heat level and arc length.

Typically, the plasma spray deposition process requires only a small amount of substrate preparation. However, because APS Materials is involved in plasma spraying parts that must perform in such hostile environments as aircraft engines (aircraft parts) and the human body (orthopedic implants), they must be assured that the plasma sprayed coating is securely adhered to the substrate. For this reason, parts that arrive at APS for coating undergo a thorough cleaning process prior to the application of the plasma spray coat.

PROCESS DESCRIPTION

ORIGINAL PROCESS

In the APS biomedical parts division, the company primarily coats cobalt/molybdenum parts and titanium parts with a porous titanium alloy. By using plasma spray technology, the porosity of the coating is controlled so that growing bone will attach to the metal surface. In order to achieve a strong and adhesive coating, the parts were cleaned with TCA or methanol (TCA for cobalt/molybdenum and methanol for titanium). TCA is more economical than methanol but weakens titanium over time. The cleaning process consists of several steps. Initially, the parts

received undergo a visual inspection for any gross defects. The parts are then partially masked with tape, exposing only the surfaces that will receive spray coating. Next, they are grit blasted to roughen the surface of the part for the application of the spray coat. After the grit blast has been completed, the masking tape is removed. The part is then immersed in a small pail containing TCA or methanol. The pail is placed in an ultrasonic bath containing warm water for 15 minutes. Solids from grit blasting, oil and grease from the manufacturing and handling of the parts, and any adhesive residuals from the masking tape are removed in this cleaning process. After the ultrasonic bath, a graphite masking suspension is applied to the part on surfaces where the plasma spray coating is not wanted. The part is then plasma sprayed and cleaned again to remove excess titanium and the graphite mask.

As a check system, APS runs small one-inch diameter disks of the same composition as the part to be coated - called "test buttons" - through the same cleaning and coating process. The test buttons are placed on a tensile strength testing machine which measures the tension required to separate the coating from the substrate as a quality control measure.

Many wastes are generated during the preparation of the part for spray coating, with TCA and methanol being the wastes of primary concern. Waste TCA and methanol were being generated at the rate of 1/2 barrel per month. Disposal of these solvents was becoming more and more difficult.

DESCRIPTION OF INITIAL BENCH SCALE EXPERIMENTS

DuSqueeze, a product of DuBois Chemicals, was selected as a possible substitute for TCA and methanol because of its disposal qualities. Disposal of dilute solutions of DuSqueeze could be accomplished by flushing it to a sanitary or industrial sewer according to local sewer use permit requirements. The feasibility of substituting a dilute, terpene-based cleaner (DuSqueeze) for TCA and methanol was determined by assessing the tensile strength of the plasma coating bonds made after cleaning with DuSqueeze. Five tests were performed, four on plasma coated test buttons to assess the tensile strength of bonds made after cleaning with DuSqueeze as compared to the tensile strength of bonds made after cleaning with methanol and TCA, and one test to determine if any limonene remained on the buttons after being cleaned. In the first test, four titanium test buttons were placed in a stainless steel beaker containing a 20:1 dilute solution of DuSqueeze and water. The solution was agitated for 20 seconds. The test buttons were then placed in a stainless steel beaker containing deionized (DI) water which was agitated for 20 seconds. The test buttons were then blow-dried and plasma sprayed. The tensile strength of the bond between the plasma arc coating and the substrate was measured using a Tinius Olsen tensile tester.

In the second test, four titanium buttons were placed in an ultrasound bath containing a 50:1 dilute solution of DuSqueeze for 10 minutes. Next the buttons were placed in a stainless steel beaker containing DI water for thirty seconds. The titanium buttons were blow dried for sixty seconds and then plasma sprayed. The tensile strength of the bonds were then tested in the same manner as the first test. The third test followed the same procedure as test two, using a 100:1 dilute solution of DuSqueeze. In the fourth test the buttons were cleaned by the same process as the third test, but the buttons were analyzed for residual limonene and were not plasma sprayed and tensile tested. In the fifth test, cobalt/molybdenum buttons were used instead of the titanium buttons with the test protocol identical to the third test.

MODIFICATIONS TO EXISTING SYSTEM

APS purchased a heated ultrasound bath with a timer for the conversion. However, when this ultrasound bath malfunctioned, a heater was added to the old ultrasound bath. The TCA/methanol cleaning system did not require a DI water rinse, so a DI water system was purchased along with a stainless steel bath and immersion heater. With the new cleaning system, the parts take longer to dry, so a heat gun was purchased to speed-up the drying process.

SAMPLING AND ANALYSIS

The overall purpose of the sampling and analysis project at APS Materials was to support a purely qualitative judgement of the cleaning capabilities of the substitute cleaning solution (i.e., DuSqueeze). The sampling and analysis protocol for this project was set up in three parts; sampling spent solutions of methanol and TCA, sampling the terpene-based cleaning solution after modifications were made to the cleaning system, and developing data for a comparative analysis of plasma coating bond strengths between the coatings of test buttons that were cleaned with methanol/TCA prior to coating and the coatings of test buttons that were cleaned with the terpene-based solution prior to coating.

PRE-MODIFICATION SAMPLING

The first part of the sampling process was performed prior to any modifications. This sampling was performed in order to determine the type and amounts of contaminants found in the cleaning solvents. Samples of the methanol and TCA cleaning solutions were taken and analyzed for oil and grease, dissolved solids, suspended solids, titanium metal and cobalt metal. This sampling also established the baseline performance for methanol and TCA. The samples were taken by mixing the material in a plastic bucket and then pouring a sample from the bucket through

a glass funnel into a glass bottle. The data derived from this sampling served as a bench mark for the ensuing DuSqueeze sampling.

POST-MODIFICATION SAMPLING

The second part of the sampling scheme was performed after the modifications were made to the system in order to determine the effectiveness of the terpene-based solvent (DuSqueeze) in cleaning the parts. Sampling of the cleaning solution was performed throughout a typical operating cycle. Samples were recovered at the beginning of a bath cycle (i.e., when the tank contents were completely replaced with fresh cleaning solution) to establish baseline concentrations. A second sample was taken midway through the effective life of the cleaning solution. A final sample was recovered prior to removing the spent solution from the dip tank.

One liquid sample was collected during each sampling episode and split into two aliquots. One aliquot was placed in a 1000-ml linear polyethylene bottle with a screw-cap lid. This sample was used to analyze for dissolved/suspended solids and the two specific metals. The second aliquot was used to test for oil and grease and was placed in a 1000-ml glass bottle with screw-cap lid. Before use, the sample containers were soap-and-water washed, rinsed thoroughly, and then soaked in acid (nitric acid for plastic, sulfuric acid for glass) for several hours. The bottles were then rinsed thoroughly with tap water, distilled water, and deionized distilled water respectively. They were air-dried and stored with their caps in place.

Preservation procedures were performed on the liquid samples immediately after sample collection. The pH of each liquid sample was measured using pH indicator paper. Acid was added to each sample until the pH was reduced to 2.0. The samples that were analyzed for dissolved/suspended solids and metals were pH-adjusted using nitric acid. Sulfuric acid was used for preserving the oil and grease samples.

In addition to taking samples of the cleaning solution, wipe samples were taken of the cleaned parts. Wipe samples were taken to evaluate the cleaning efficiency of the solution over time by analyzing for residual contaminants (oil and grease) on the parts. One wipe sample was taken from the cleaned metal parts during each sampling interval to determine if there was a residual of oil and grease. The wipe sample was performed using sterile, uncontaminated cloth. Sterile gloves were worn to prevent contamination of the cloth with oil and grease. The wiping procedure was consistent for each sample. A glass container of sufficient volume was used to hold the cloth after sampling. Three wipe samples were taken over the life of the DuSqueeze cleaning solution, to coincide with the three liquid samples described above.

Analysis for metals was performed using inductively-coupled plasma atomic emission spectroscopy (ICP). Oil, grease and dissolved/suspended solids were analyzed using gravimetric analytical techniques. Spikes and replicate analyses were also done to check for accuracy and precision and to identify the presence of any matrix effects associated with sample preparation or measurement. Data were then combined and statistically evaluated.

The analysis of plasma coating bond strength compared current data collected by APS Materials regarding the strength of coatings applied after parts were cleaned with DuSqueeze and historical data of bond strength resulting from parts cleaning with TCA and methanol. Data generated two months prior and two months following the conversion to DuSqueeze were used for this comparison.

RESULTS AND DISCUSSION

BENCH SCALE EXPERIMENTS

The before and after tensile strength results were comparable. Overall, the bonding strengths were actually slightly better for the dilute limonene cleaner (see Table 1). No residual limonene was detected (detection limit 1 ppm) for cleaner at 100:1 dilution.

TABLE 1. TENSILE STRENGTH TEST RESULTS FOR BENCH SCALE EXPERIMENTS

Test Buttons	Cleaning Agent	Tensile Strength (psi)
titanium	methanol	6300+/-1260
titanium	DuSqueeze*	7000+/-570
cobalt/molybdenum	TCA	5150+/-1990
cobalt/molybdenum	DuSqueeze*	5400+/-1290

* Tensile strengths measured for test button cleaned with various dilutions of DuSqueeze showed no trends or statistical differences, so values shown include all measurements.

ANALYSES FOR IN-PLANT OPERATIONS

The initial tests for contaminants in methanol and TCA used for cleaning yielded the results shown in Table 2. The samples for these analyses were taken when the baths were considered spent, just prior to being dumped.

TABLE 2. RESULTS OF ANALYSES OF SOLVENT SAMPLES FOR CONTAMINANTS

Test	Methanol (mg/L)	TCA (mg/L)
Dissolved solids	1	29
Suspended solids	33	9
Oil and Grease	911	141
Metals		
Cobalt	-	ND
Titanium	0.021	-

* Method detection limit is 0.01

The amounts of oil and grease found in the wipe samples, shown in Table 3, were very low at about 1 mg or less. The increase in oil and grease from the bath dump as compared to the fresh bath was very small for one sample and was less than the fresh bath in the second bath dump sample. This latter result could have resulted from the wiping technique. In any case, the parts seem to be cleaned just as well at the time the bath is dumped as when the bath is fresh.

TABLE 3. RESULTS OF ANALYSES FOR OIL & GREASE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	Oil and Grease Total Mg
Wipe Sample, Fresh Bath	1.0
Wipe Sample, Mid-life Bath	0.4
Wipe Sample, End-life Bath	1.2
BLANK	ND*

* Method detection limit is 0.3

Table 4 shows results from analyses for residual limonene on the parts. Limonene was not detected in the rinse samples, thus indicating that all of the limonene was removed during dragout and subsequent drying of the parts.

TABLE 4. RESULTS OF ANALYSES FOR RESIDUAL LIMONENE ON PARTS CLEANED WITH 100:1 DILUTE SOLUTION DUSQUEEZE

Test	limonene concentration Total Uq/sample
Rinse Sample, Fresh Bath	ND(<0.3)
Rinse Sample, Mid-life Bath	ND(<0.65)
Rinse Sample, End-life Bath	ND(<0.3)
BLANK	ND(<0.2)

In comparing the results in Table 5, it is noted that dissolved solids and oil and grease were much higher in the fresh bath and the bath used to clean parts only prior to plasma spraying (Dump#1), than in the bath used also for cleaning after plasma spraying (Dump#2), while the reverse was true for the suspended solids. The graphite in the bath may affect the DuSqueeze cleaning solution to create these differences.

TABLE 5. RESULTS OF ANALYSES OF 100:1 DILUTE DUSQUEEZE SOLUTION FOR CONTAMINANTS

Test	Fresh Bath mg/L	Dump#1 mg/L	Dump#2 mg/L
Dissolved solids	3650	3010	887
Suspended solids	ND*	ND*	19
Oil and Grease	37.0	30.8	15.1
Metals			
Cobalt	0.019	0.18	0.081
Titanium	ND#	ND#	1.65

* Method detection limit is 2

Method detection limit is 0.047

In comparing the DuSqueeze cleaning solution with the previous methanol and TCA samples, it is noted that the oil and grease levels in the DuSqueeze are much lower than the other cleaning solvents. Suspended solids for the DuSqueeze are lower than the previous solvents except for the sample containing graphite which is roughly equivalent. Dissolved solids for DuSqueeze are much higher than the other solvents.

The higher dissolved solids may reflect the fact that the DuSqueeze is an emulsifying agent which converts the oil and grease to dissolved solids. This would explain the lower oil and grease levels for DuSqueeze.

TABLE 6. TENSILE STRENGTH TEST RESULTS FOR IN-PLANT OPERATIONS

Coating/Substrate	Cleaning Agent	Tensile Strength (psi)
titanium / titanium	methanol	5560+/-600
titanium / titanium	DuSqueeze	7180+/-610
titanium / cobalt-moly	TCA	5820+/-370
titanium / cobalt-moly	DuSqueeze	5330+/-1560

Although the data generated by the sampling and analysis program, shown in Table 6, indicate that the terpene-based cleaner adequately cleaned the parts for this process, since wipe samples were not taken for the original process, a statement of comparison between the former and present cleaning techniques is not feasible.

ECONOMIC ANALYSIS

Although the old ultrasound bath was in use at the time of the test, economic analysis is shown for the system that APS is now operating.

- Capital Cost: Ultrasound with heater \$1425
 5-gallon stainless rinse vessel \$38
 Immersion heater \$105
 Heat Gun \$75
 DI water system installation \$150
 TOTAL - \$1793
- Annual operating costs: 7.8-11.8 gal DuSqueeze \$150
 1825-2920 gal DI water \$700
- Cost savings from avoided purchases:
 330 gal TCA \$1650
 120 gal methanol \$1000
- Cost savings from avoided disposal: 6 barrels \$3000
- Net Cost savings: \$4800 a year
- Payback $\$1793/\$4800 = 0.37$ year, 4.5 months

CONCLUSIONS

In summary, it has been determined that a terpene-based cleaner can adequately clean metal parts without adversely affecting the performance of the plasma-arc coating application. The use of a terpene-based cleaner in place of methanol and TCA has proven to be an environmental and economic success. Elimination of the disposal problems associated with methanol and TCA coupled with the maintenance of plasma-arc coating quality makes the use of terpene-based cleaners attractive to other plasma spray coating processes as well as other metal cleaning/coating operations. The annual cost savings as well as the short payback period also make the cleaner attractive from an economic standpoint.

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WASTE MINIMIZATION ASSESSMENT CENTERS

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ABSTRACT

In 1988, University City Science Center (Philadelphia, Pennsylvania) began a pilot project to assist small and medium-size manufacturers who want to minimize their formation of hazardous waste but who lack the in-house expertise to do so. Under agreement with the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency, the Science Center's Industrial Technology and Energy Management (ITEM) division established two waste minimization assessment centers (WMACs) at Colorado State University in Fort Collins and at the University of Tennessee in Knoxville. During the second program period of the project, a third WMAC established at the University of Louisville (Kentucky) has begun to conduct assessments.

Each WMAC is staffed by engineering faculty and students who have considerable direct experience with process operations in manufacturing plants and who also have the knowledge and skills needed to minimize hazardous waste generation. The waste minimization assessments are conducted at no out-of-pocket cost to the client. Several site-visits are required for each client served. The WMAC staff locate the sources of hazardous waste in each plant and identify the current disposal or treatment methods and their associated costs. They then identify and analyze a variety of ways to reduce or eliminate the waste. Specific measures to achieve that goal are recommended and the essential supporting technological and economic information is developed. Finally, a confidential report which details the WMAC's findings and recommendations including cost savings, implementation costs, and payback times is prepared for each client manufacturer.

This presentation will discuss results from the first period of this project.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

WASTE MINIMIZATION ASSESSMENT CENTERS

INTRODUCTION

The amount of hazardous waste generated by industrial plants has become an increasingly costly problem for manufacturers and an additional stress on the environment. One solution to the problem of hazardous waste is to reduce or eliminate the waste at its source.

University City Science Center (Philadelphia, Pennsylvania) has begun a pilot project to assist small and medium-size manufacturers who want to minimize their formation of hazardous waste but who lack the in-house expertise to do so. Under agreement with the Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency, the Science Center's Industrial Technology and Energy Management (ITEM) division initially established two waste minimization assessment centers (WMACs) at Colorado State University in Fort Collins and at the University of Tennessee in Knoxville. Each WMAC is staffed by engineering faculty and students who have considerable direct experience with process operations in manufacturing plants and who also have the knowledge and skills needed to minimize hazardous waste generation. During late 1989, a third WMAC at the University of Louisville was established.

During the initial period of this pilot project, each of the two WMACs conducted six assessments for small and medium-size manufacturers at no out-of-pocket cost to the client. Each client had to meet the following criteria:

- Standard Industrial Classification Code 20-39
- Gross annual sales of not more than \$50 million
- No more than 500 employees
- Lack of in-house expertise in waste minimization

The potential benefits of the pilot project include minimization of the amount of waste generated by manufacturers, reduced waste treatment and disposal costs for participating plants, valuable experience for graduate and undergraduate students who participate in the program, and a cleaner environment without more regulations and higher costs for manufacturers.

All told, the measures recommended by the two WMACs in these 12 plants accounted for an identified cost saving of \$1.28 million/year. This paper describes how the cost savings were found and identifies the specific measures designed to reduce waste formation and emissions from two of these plants. However, equally detailed accounts of the other ten plants could also be prepared.

METHODOLOGY OF ASSESSMENTS

The waste minimization assessments require several site-visits to each client served. In general, the WMACs follow the procedures outlined in the Waste Minimization Opportunity Assessment Manual, July 1988. The WMAC staff locate the sources of hazardous waste in each plant and identify the current disposal or treatment methods and their associated costs. They then identify and analyze a variety of ways to reduce or eliminate the waste. Specific measures to achieve that goal are recommended and the essential supporting technological and economic information is developed. Finally, a confidential report which details the WMAC's findings and recommendations including cost savings, implementation costs, and payback times is prepared for each client manufacturer.

RESULTS

PLANT No. 1 (SIC 2851)

This plant produces paints, coatings, stains, and surface-treating products at an overall rate of about 1.1 million gallons/year for regional distribution on a schedule of 2080 hours/year for 52 weeks. Its operations primarily involve blending and mixing of raw materials, followed by product testing and packaging and by cleaning of vessels and lines. Color separation in the product is obviously important, and each lot must meet a variety of other customer specifications.

Plant Operations

Individual lots of water-based and solvent-based paints are mixed in a variety of tanks from 200 to 1000 gallons' capacity. Ingredients for this initial step include (for water-based) water, latex, resins, extenders, and dispersed pigments. For solvent-based paints the materials are generally similar in type, but obviously solvent replaces water and latex, and the other new ingredients include plasticizers, tints, and thinners.

After batches are made up they are transferred to so-called let-down tanks, where additional water (or solvent), resins, preservatives, anti-foaming agents, thinners, and bactericides are added. Testing of batches encompasses at least color, viscosity, and gloss, and those lots which meet specifications are filtered and charged to cans for labeling, packaging, and shipping.

Waste Generation and Existing Waste Management Practices

The principal waste streams are the result of equipment cleaning, especially from water-based paints. For example, rinsing the let-down tanks ordinarily requires about 35 gallons of rinse water, but that value increases to 53 gallons if light paint is to be blended after a dark predecessor. The hazardous nature of water rinses is due to mercury from the bactericide in the paint.

In some instances, rinse water from the mixing tanks is held in 500-gallon tanks and used in the let-down tanks (instead of fresh water) to formulate future batches of water-based paint. The rinses are separated according to the color intensity of paint in the tanks from which they were derived. For example, rinses from white paint formulation amount to about 70% of the total, and they are invariably used again.

Waste rinses not used again are piped to holding and flocculation tanks, to which alum is added to lower the pH, in which some solid is precipitated by adding flocculant, and from which supernatant liquid is removed for re-use in other paint formulations.

Tanks used for solvent-based paints are rinsed with mineral spirits at a rate of about 5 gallons/400-gallon tank. These washings are sent off-site for recovery, followed by recycling or sale as fuel.

In addition to re-use of rinse water and recovery of solvent, this plant has adopted the following measures to reduce waste generation:

- Cleaning equipment before the paint dries and hardens.
- Eliminating hazardous materials, except for mercury in the bactericide added to outdoor water-based paint.
- Avoiding hazardous container waste by purchasing the bactericide in water-soluble bags which dissolve during paint formulation.
- Scheduling batch formulations so that light ones precede dark ones and thereby reduce the total volume of rinses.

- Reducing the inventory of raw materials to avoid degradation and spoilage and to assure high-quality product that can be sold, rather than low-quality paint which adds to the burden of waste disposal.
- Using bag filters to collect dust.

Waste Minimization Opportunities

Table 1 summarizes the principal sources of waste, their amounts, the management method applied, and the associated costs.

Table 2 offers a brief description of each recommended WMO (Waste Minimization Opportunity) and of current plant practice, together with savings and cost data. Considered individually, the three WMOs recommended could save over \$22,000/year, which represents about 25% of current waste management costs. Each has a simple payback time less than one year.

PLANT No. 2 (SIC 3443)

This plant manufactures aluminum brazed oil coolers for use in heavy equipment. It produces approximately 59,290 units each year.

Manufacturing Operations

The raw materials used in the production of the oil coolers include aluminum in sheet and coil form, aluminum castings and extrusions, tubes, fittings, brackets, caution labels, and plastic plugs.

The following steps are involved in production:

- Shearing, punching, and forming operations to fabricate the oil cooler tanks, headers, air fins, sides, and oil turbulator fins.
- Degreasing of oil cooler tanks, headers, sides, fittings, and brackets. The solvent Chlorothene (95% 1,1,1 - trichloroethane) is used in an open-air, steam-heated vapor degreaser. The unit is equipped with a refrigeration unit which condenses Chlorothene vapor and minimizes evaporative losses to surrounding plant air.
- Recycling of spent Chlorothene to the degreasing operation using an on-site still. Chlorothene is continuously circulated between the degreaser and a steam-heated solvent recovery still. Still bottoms containing spent Chlorothene, water, and oil are shipped off-site as hazardous waste.
- Assembly of oil coolers.
- Brazing of assembled oil coolers to join the internal and external coil fin surfaces for enhanced heat transfer. The oil coolers are first preheated in a gas-fired oven at 1020° F for 15 minutes. They are then dipped into an electrically-heated molten salt bath containing a sodium chloride-based compound, lithium chloride, and aluminum fluoride for 1 1/2 minutes at 1128° F and dipped in a water quench tank. Sludge from the salt bath and quench tanks is disposed in the outdoor on-site sand filter bed. Solids remaining in the filter are landfilled on company property; water is fed to the settling pond and eventually discharged to a river.
- Cleaning of oil coolers to remove all residual salt, expose copper cells (which could cause corrosion failure), and condition metal surface prior to painting. The following steps are involved in the cleaning:
 - submersion in a 2% nitric acid bath (1-2 hour residence time)

TABLE 1. SUMMARY OF WASTE GENERATED (SIC 2851)

WASTE STREAM	WASTE TREATMENT		WASTE DISPOSAL	
	Amount	Cost	Amount	Cost
HAZARDOUS LIQUID WASTE				
A. Water-based Waste:				
Equipment cleaning by water washing	26,700 gal (Hg water and paint)	\$3,740	26,700 gal off-site	\$48,040
B. Solvent-based Waste:				
Equipment cleaning by solvent washing			27,200 gal (mineral spirits) off-site	\$37,080
TOTALS	26,700 gal	\$3,740	53,900 gal	\$85,120

TABLE 2. SUMMARY OF WASTE MINIMIZATION OPPORTUNITIES RECOMMENDED (SIC 2851)

WHO No.	Present Practice	Proposed Action	Cost Savings
1	Water rinses remove paint from tanks and pipes	Install a pipe-cleaning system consisting of 3 different-sized foam plugs or "pigs" to be sent throughout the pipes by compressed air. Paint is thus forced from the lines and to the canning line filter. The use of water and amount of waste are lower. (This WHO is applicable to non-white paints.)	- Estimated waste reduction - 1,780 gal/yr - Estimated cost reduction - \$11,110/yr - Estimated implementation cost - \$1,600 - Simple payback - 2 months
2	About 15 gal solvent per batch of paint is drummed and sent off-site for disposal.	Use a solvent recovery system based upon distillation and ship the small amount of remaining solid to a hazardous waste disposal site.	- Estimated waste reduction - 3,300 gal/yr - Estimated cost reduction - \$5,420/yr - Estimated implementation cost - \$4,950 - Simple payback - 11 months
3	A bactericide containing mercury is being used in water-based paints.	Eliminate the bactericide from water-based interior paints and substitute an organic material. (This WHO is applicable to non-white paints.) There is no cost difference between these additives.	- Estimated waste reduction - 3,100 gal/yr - Estimated cost reduction - \$5,580/yr - Estimated implementation cost - none - Simple payback - immediate

- cold water rinse
 - dipping in NaOH caustic soda etching solution
 - hot water (102°F) rinse
 - cold water rinse
 - dipping in a 50% nitric acid bath
 - 2 cold water rinses
 - dipping in a chromic acid wash
 - 2 de-ionized water rinses
 - drying in a natural gas-fired oven
- Treatment of hazardous spent process solutions and contaminated rinse water streams. The liquids are treated in a neutralization tank with lime for pH control and flocculant to enhance removal of suspended solids. The solution leaving the tank is pumped to a clarifier which removes solids and allows filtered water to flow to the settling pond. A solids-rich stream is pumped to a sludge-thickener settling tank for secondary sedimentation. Supernate from the settling tank is transferred to the sand filter beds for final water removal before on-site landfilling of solids.
 - Treatment of effluent from the chromic acid and de-ionized rinse water washes. These hazardous waste streams contain chromium in hexavalent form. The streams are treated to obtain a sludge containing less toxic trivalent chromium compounds. Several chemical agents are added to the waste to produce relatively insoluble compounds which are recovered on the sandfilter beds and disposed in the landfill. The liquid is pumped to the settling pond and is eventually released to the river.
 - Painting of oil coolers. The coolers are dipped in a paint-filled tank, allowed to drip after immersion, and transferred to a spray booth for additional spray painting. Paint is collected on floor coverings (plastic sheet or cardboard) and in spray booth filters and disposed of daily in barrels which are sent to an off-site landfill.

Existing Waste Management Practices

The plant has taken the following steps in managing its hazardous wastes.

- The plant owns and operates a landfill for its private use.
- Chromium reduction from hexavalent to trivalent form is performed in-house.
- A refrigeration unit and a solvent recovery still have been added to the degreasing unit to minimize evaporative loss and liquid waste.
- The plant constantly monitors its waste-stream effluents and has installed its own hazardous waste treatment facility.
- Water-based paints are currently used.
- The plant has a designated professional staff person based at corporate headquarters who periodically visits satellite plant locations to provide assistance in both hazardous waste monitoring and management techniques.

Waste Minimization Opportunities

The waste currently generated by the plant, the source of the waste, the quantity of the waste, and the annual treatment and disposal costs are given in Table 3.

Table 4 shows the opportunities for waste minimization that the WMAC recommended for the plant. The waste in question, the minimization opportunity, the possible waste reduction and associated savings, and the implementation cost along with the payback time are given.

TABLE 3. SUMMARY OF WASTE GENERATED (SIC 3443)

Waste Generated	Source of Waste	Quantity Generated	Annual Waste Management Cost
Still bottoms containing spent, contaminated Chloroethene (95% Chloroethene, water, and oil).	On-site solvent recycling still associated with the degreasing operation.	150 gal/yr	\$4,650
Evaporation of Chloroethene	Degreasing operation.	6,325 gal/yr	0(a)
Sludge containing compounds derived from the salt bath constituents, impurities from the baths, and contaminants on the products' surfaces.	Salt bath tank and water quench tank in the brazing process. The sludge is collected on the sand filter beds.	514.917 lb/yr	28,600
Sludge containing various solvents from the treatment of the spent cleaning solutions.	Treatment process for spent solutions from the cleaning of the brazed product. The sludge is collected on the sand filter beds.	1,171.060 lb/yr	36,375
Sludge containing various compounds from the chromium reduction process.	Chromium reduction process. The sludge is collected on the sand filter beds.	88,943 lb/yr	16,500
Paint-contaminated filters and cardboard and plastic sheets.	Painting of product.	9.812 lb/yr	12,495

(a) Currently there are no waste management costs associated with the evaporation of Chloroethene.

TABLE 4. SUMMARY OF WASTE MINIMIZATION OPPORTUNITIES RECOMMENDED (SIC 3443)

Part I

Waste	Minimization Opportunity	Waste Reduction Quantity	Waste Reduction Per Cent	Net Annual Savings	Implementation Cost	Payback Years
Evaporation of Chloroethene from the degreaser unit.	Install a conveniently removable cover on the vapor degreaser tank to reduce evaporative losses. Cover the tank except during times when parts baskets are being lowered into or taken out of the tank.	3,263 gal/yr	50%	\$17,180(A)	\$220	0.01
Still bottoms from the on-site solvent recycling still.	Reduce the amount of lubricants used during metal-working and the openness of machine work areas to decrease the amount of oil picked up by parts during processing, thereby minimizing the amount of degreasing required.	30 gal/yr	20%	1,010(A)	290	0.3
Evaporation of Chloroethene and Chloroethene contained in the still bottoms.	Replace the vapor degreaser system with an ultrasonic cleaning system which utilizes biodegradable detergents.	6,600 gal/yr	99%	20,450(B)	50,000	2.4
Sludge from the water quench tank in the brazing process.	Modify the procedure for dipping the coolers in the salt bath to minimize carry-over to the water quench tank. Achieve maximum salt removal by gently vibrating or shaking the parts baskets and subjecting the parts to a hot air blast.	23,171 lb/yr	4%	20,520(C)	43,880	2.1
Sludge from the salt bath and water quench tanks in the brazing process.	Replace molten salt bath brazing with vacuum brazing. Vacuum brazing is suitable for 80% of this plant's products.	411,934 lb/yr	80%	203,440(C)	720,640	3.5

TABLE 4. SUMMARY OF WASTE MINIMIZATION OPPORTUNITIES RECOMMENDED (SIC 3443)

Part II

Waste	Minimization Opportunity	Waste Reduction Quantity	Per Cent	Net Annual Savings	Implementation Cost	Payback Years
Paint-contaminated cardboard and plastic sheets.	Reduce paint loss by installing a low-pressure air-jet system over the paint dipping area to blow excess paint downward into tank. Install an IR paint- drying lamp to prevent dripping when coolers are moved to the spray booth area.	2,180 lb/yr	22%	4,350 (D)	2,490	0.6
Paint-contaminated filters and cardboard and plastic sheets.	Install an electrostatic spray paint system for application of the oil cooler second coat of paint in order to reduce overspray loss.	3,513 lb/yr	36%	11,200 (D)	13,200	1.2
Paint-contaminated filters and cardboard and plastic sheets.	Discontinue the practice of painting oil coolers which will be re-painted by the customer.	4,906 lb/yr	50%	59,720 (D)	28,440	0.5

- (A) Includes cost savings attributed to the avoided purchase of Chlorothene.
 (B) Total savings have been reduced by the cost of detergents required.
 (C) Includes cost savings attributed to the avoided purchase of salt bath constituents.
 (D) Includes cost savings attributed to the avoided purchase of paint supplies.

DISCUSSION OF RESULTS

The two plants described have annual waste management costs of \$188,370 and the WMACs were able to recommend to them a series of cost-saving measures which add up to \$359,980 per year. The savings total exceeds the aggregate waste management cost because, in one of the two plants, the measures recommended save more than the cost of waste treatment, disposal, and recycling.

For example, in plant No.2, only a \$13,485 waste management cost is presently associated with paint-contaminated filters and cardboard and plastic sheets but elimination of the painting is estimated to save almost \$60,000 per year. Typically, savings in raw materials costs of 25 to 80% can be achieved by the recommendations offered. It is not hard to see how this kind of savings can add up to more than the costs of waste management in some plants.

The cost-saving approach taken with these results is generally conservative, because the WMOs address only the avoidance of raw materials costs and the reduction of present and future costs associated with waste treatment and disposal. Not claimed are the savings related to: possible changes in emission standards, any liability incurred from waste management practices, and costs arising from employee health and safety problems. It should also be noted that each WMO identified is treated as an isolated individual measure and no consideration has been given to effects occurring because of interactions among WMOs.

The WMAC program is continuing to serve eligible manufacturers, and future results are expected to allow more generalizations about the amounts and types of industrial waste materials encountered in the nation's plants.

It seems reasonable to conclude from recent WMAC program experience that small and medium-size manufacturers:

- Have recognized many of their waste generation problems and have undertaken a variety of actions to address them.
- Are receptive toward practical quality assistance, offered in their plants objectively and competently, that can help them to choose cost-effective waste minimization opportunities over and above what they have been able to achieve on their own.

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VETERANS AFFAIRS HOSPITAL AND HOSPITAL WASTE MINIMIZATION CASE STUDIES

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ABSTRACT

The U.S. Environmental Protection Agency has instituted a broad pollution prevention research program through the Office of Research and Development to support continued environmental improvements throughout the nation. The Agency is also responding to the national concern in regards to the generation and disposal of medical wastes. Recently, EPA's Risk Reduction Engineering Laboratory (RREL) produced the "Guide to Waste Minimization in Selected Hospital Waste Streams" (1) with the cooperation of the California Department of Health Services (hereafter referred to as the "California Study"). The California Study serves as a manual for conducting waste minimization assessments at surgical and general medical hospitals to reduce the generation of hazardous wastes from chemotherapy and antineoplastic chemicals, formaldehyde, photographic chemicals, radionuclides, solvents, mercury, anesthetic gases and other waste chemicals.

In order to effectively implement its pollution prevention programs, the EPA is also investigating how the departments and agencies within the Federal community can help each other reduce their generation of wastes. As a part of these efforts, RREL provides staff and support to conduct waste minimization assessments under the Waste Reduction Evaluations and Assessments at Federal Sites (WREAFS) Program. Under the WREAFS program, the U.S. Department of Veterans Affairs Cincinnati - Fort Thomas Medical Center (DVA-Cin) offered to host an assessment of pollution prevention opportunities at their facility (2). With the California Study having researched the generation of hazardous wastes in hospital settings, the DVA-Cin Study investigated the use of disposables in patient care in order to identify research opportunities for future solid waste minimization.

During the assessment it became clear that DVA-Cin, driven by its sensitivity to health care costs, has in place some very effective waste minimization practices. Unlike most hospitals, DVA-Cin does not have access to private insurance and therefore cannot assign costs on a per bed basis. As a result, the generation of medical waste is well below the average level for a hospital of this size.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

VETERANS AFFAIRS HOSPITAL AND HOSPITAL WASTE MINIMIZATION CASE STUDIES

INTRODUCTION

The California Study and the DVA-Cin Study represent RREL's initial efforts in the research of hospital wastes. Together, the studies profile those wastes that are unique to medical care facilities: hazardous and bio-hazardous wastes, wastes generated from patient care, and medical laboratory wastes. RREL did not attempt to study wastes generated in other areas of the hospitals (e.g., office settings, cafeteria, plant maintenance), as these wastes are common to many non-medical facilities which have been examined in prior studies.

This paper will outline the waste profile of medical care facilities and suggest waste minimization options based upon the results of both the California and DVA-Cin Studies. This will include a discussion of research needs/opportunities derived from the DVA-Cin Study.

THE CALIFORNIA STUDY

HAZARDOUS WASTE PROFILE

While the volumes of hazardous wastes generated are small in comparison to an industrial facility, hospitals do employ a wide variety of toxic chemicals and hazardous materials for numerous diagnostic and treatment purposes. Based on the assessments of three hospitals under the California study, the highest volume of hazardous waste generation comes from the use of chemotherapy and antineoplastic chemicals, followed by spent photographic chemicals and formaldehyde solutions used for disinfecting equipment. Briefly, the wastes studied include:

Chemotherapy and Antineoplastic Chemicals - Antineoplastic, or cytotoxic, agents are typically kept on hand in quantities sufficient to last two weeks. To produce chemotherapy solutions, chemicals are mixed under a hood which recirculates air through a filter. Only a small percentage of these wastes contain concentrated amounts of chemotherapy compounds. Much of the waste is associated with lightly contaminated items such as personal protective clothing and gauze pads. An average of 2 to 8 cubic feet of chemotherapy wastes were generated weekly by the hospitals surveyed. These wastes were either transported off-site to a Class I landfill or incinerated as hazardous waste. It should be noted that individual States have differing regulations

on how such waste is to be disposed. What is allowed in one State may be a violation in another. Therefore, the waste minimization recommendations that are made in this paper have to be taken in light of the medical waste regulations of the State in which the hospital is located.

Formaldehyde - Formaldehyde is used in pathology, autopsy, dialysis, embalming, and nursing units. For use in dialysis, formaldehyde is generally purchased as a 37 percent solution (formalin) that will be diluted with filtered, de-ionized water to a final formaldehyde concentration of 2-4 percent. Formaldehyde is used to disinfect membranes in dialysis machinery and, in other departments, to preserve specimens. Effluent is commonly discharged to a sewer, although in some States this may be considered an illegal practice.

Photographic Chemicals - Photographic developing solutions consist of three parts: developer, stop bath, and fixer. The developer normally contains approximately 45 percent glutaraldehyde. Acetic acid is a component of stop baths and fixer solutions. The fixer will contain 5-10 percent hydroquinone, 1-5 percent potassium hydroxide, and less than 1 percent silver. Silver-containing effluent is typically passed through a steel wool filter or electrowinning unit to recover the metal. The remaining aqueous waste, containing approximately 1.4 percent glutaraldehyde, 0.3 percent hydroquinone, and 0.2 percent potassium hydroxide, is typically discharged to the sewer.

Radionuclides - Radioactive wastes are generated in nuclear medicine and clinical testing departments. At the hospitals surveyed, radioactive materials in nuclear medicine were held on-site until they decayed to non-hazardous levels. In clinical testing laboratories, solvents were used for radioactive tagging. Wastes at the hospitals were generated at the rate of 800 cubic centimeters per week. Radioactive wastes were transported off-site to a landfill.

Solvents - Solvent wastes are generated in small amounts in various departments: pathology, histology, engineering, embalming, and laboratories. A variety of halogenated and non-halogenated compounds are used, but, in the hospitals surveyed, the most frequently used solvents were non-halogenated: xylene, methanol, and acetone. While acetone and methanol wastes are usually evaporated and/or discharged to a sewer, xylene is handled as a hazardous waste. Solvent wastes are typically recycled or transported off-site for incineration. However, some solvent wastes become absorbed into the specimen and then must be treated as infectious wastes. In the past, small quantities of solvent waste would be routinely disposed via lab packs to landfills. However, high disposal costs, long term liability and regulatory limitations make this an undesirable disposal alternative.

Mercury - Mercury wastes are primarily generated by broken or obsolete equipment. Spilled mercury can be recovered and reused if uncontaminated, however, spillage is not frequently recovered and no mercury spill kits were present in any of the surveyed hospitals.

Anesthetic Gases - Nitrous oxide and the halogenated agents halothane (Fluothane), enflurane (Ethrane), isoflurane (Forane), and other substances are used as inhalation anesthetics. Nitrous oxide is supplied as a gas in cylinders and used containers are returned to the supplier for refill. The

halogenated agents are supplied in liquid form, in glass bottles. Once empty, the bottles are treated as hazardous waste. Waste anesthetic gases are vented from the operating room directly to the outside, or through a charcoal filter. Spent charcoal filters are transported off-site and disposed of as hazardous waste.

HAZARDOUS WASTE MINIMIZATION OPTIONS

As a result of the hospital assessments, a series of waste minimization options were developed for the wastes categorized above, as well as some other wastes not addressed by this paper. These options are briefly portrayed in Table 1.

While the waste minimization options listed on Table 1 respond to specific waste streams, better operating practices are essential to hospital-wide waste reduction. Better operating practices are procedures and institutional policies that result in a reduction of waste, and are exhibited through such pollution prevention measures as:

Waste Stream Segregation - It is important to keep hazardous waste segregated from non-hazardous waste since all materials that come into contact with hazardous waste becomes hazardous. Hazardous chemical wastes should be kept separate from infectious wastes. Further, dilution of hazardous waste should be avoided, as it only increases the volume of waste that will have to be treated as hazardous. Finally, recyclable materials should be segregated from non-recyclable waste.

Monitoring Procurement and Product Flow - By centralizing the purchasing and dispensing of drugs and other hazardous chemicals, a facility can more readily recognize the occurrence of unnecessary waste and spillage, while assessing opportunities to minimize usage. Monitoring drug and chemical flows from receipt to disposal can be achieved through the use of automated data systems and bar-coding similar to that used in supermarkets. In addition to improving tracking and control, such a system may also provide cost savings by allowing the hospital to carry lower stocks in inventory efficiently.

Integrating Individual Departments with Waste Management Responsibilities - Apportion waste management costs to the departments generating the wastes, and require users of chemicals with limited shelf life to use up old stock before ordering new and to report on expired stock.

Training Employees and Providing Necessary Equipment - Employees should be trained in hazardous materials management and waste minimization. Employees need to be aware of chemical hazards, how to prevent spills, how to provide adequate maintenance of equipment, and how to remediate spills quickly and safely.

TABLE 1. WASTE MINIMIZATION METHODS
FOR GENERAL AND SURGICAL HOSPITALS

WASTE CATEGORY	WASTE MINIMIZATION METHOD
Chemotherapy and Antineoplastics	> Optimize drug container sizes in purchasing. > Return outdated drugs to manufacturer. > Centralize chemotherapy compounding location. > Minimize waste from compounding hood cleaning. > Provide spill cleanup kits. > Segregate wastes.
Formaldehyde	> Minimize strength of formaldehyde solutions. > Minimize wastes from cleaning dialysis machinery. > Use reverse osmosis water treatment to reduce dialysis cleaning demands. > Capture waste formaldehyde. > Investigate reuse in pathology, autopsy labs.
Photographic Chemicals	> Return off-spec developer to manufacturer. > Cover chemical tanks to reduce evaporation. > Recover silver efficiently. > Use squeegees to reduce bath losses. > Use counter-current washing.
Radionuclides	> Use less hazardous isotopes whenever possible. > Segregate and label radioactive wastes, and store short-lived radioactive wastes on-site until decay permits disposal as general trash.
Solvents	> Substitute less hazardous cleaning agents. > Reduce analyte volume requirements. > Use pre-mixed kits for tests involving solvent fixation. > Use calibrated solvent dispensers for routine tests.
Mercury	> Substitute electronic devices for mercury-containing devices. > Provide spill cleanup kits and personnel training. > Recycle uncontaminated mercury wastes.
Waste Anesthetic	> Employ low-leakage work practices. > Purchase low-leakage equipment. > Maintain equipment to prevent leaks.

THE DVA-CIN STUDY

The fact that hospital and medical care costs have risen dramatically throughout this decade is commonly attributed to the cost-plus-fee reimbursement structure of medical insurance. Under this system, the health care facility is able to pass on direct costs, a portion of overhead costs, and service fees to each patient for eventual reimbursement by an insurance carrier following an established rate scale. Since the insured patient does not feel the full impact of the cost of services received, the health care facility has had little direct incentive to reduce those costs, and probably even less incentive to investigate the cost benefits from incorporating pollution prevention opportunities. However, DVA facilities are not reimbursed for health care services; each facility operates under a budget fixed by the Department of Veterans Affairs for the fiscal year. Therefore, individual facilities such as DVA-Cin are very sensitive to cost, since achieving cost savings translates into an ability to extend their services.

Since the California Study had previously emphasized the opportunities for hazardous waste minimization, RREL and DVA-Cin chose to look for pollution prevention alternatives for minimizing the discarded medical supply wastestream. That the VA-Cin is uniquely suited to such a study is directly attributable to its cost sensitivity. The need to deliver services under a fixed budget has led DVA-Cin to both adopt environmentally clean practices on its own, and to continue clean practices that cost-reimbursement hospitals had abandoned. For example, the DVA-Cin Medical Center carefully segregates its waste in order to minimize the volume that will have to be transported by the infectious waste hauler (unit costs for infectious waste disposal far exceed those of general refuse). Also, taking advantage of its access to a DVA operated laundry in Dayton, Ohio, DVA-Cin still uses durable cloth gowns and drapes instead of the disposable paper variety. Hospital staff who indicated having prior work experience with other Cincinnati area hospitals maintained that DVA-Cin's consumption of disposable gowns and drapes was the lowest in the metropolitan area.

DISPOSABLE MEDICAL SUPPLIES

The use of disposables in hospitals and the medical profession has increased steadily over the past thirty years as devices and items constructed of metal, glass, and fabric have been replaced with plastic and paper materials intended to be used once, and then discarded. There are four major factors that explain this preference for disposables:

Health and Safety - Products that arrive prepackaged and pre-sterilized reassure medical professionals of their integrity, and eliminate the burden of monitoring inhouse re-sterilization procedures.

Cost - Disposables lower inhouse labor costs and manpower associated with cleaning, re-sterilizing and wrapping durable devices and products.

Convenience - Such things as disposable operating room (OR) packs provide all the sterile materials needed for a specific operation, reducing OR prep time.

Space Constraints - Only needed materials are kept in stock, and there is no need to review inventory for aging and obsolete items.

DISPOSABLE WASTE PROFILE

The majority of waste generated by a hospital consists of disposable products. According to DVA-Cin personnel, approximately 80 percent of the hospital's supplies are disposed after a single use. The DVA-Cin saw a change from reusables to disposables 10-15 years ago and an additional increase in the use of disposables in the last 2-3 years due to concern by hospitals over both patient safety and staff occupational exposure to the AIDS virus. Therefore, the increase results from greater usage of existing disposable supplies (i.e., single-use sponges for patient surgery, and disposable gloves and masks worn to protect hospital staff) rather than from the use of newly developed disposable items.

This section will profile the major disposable items ordered by these DVA-Cin departments: Laboratory Services; Surgery; Surgical Intensive Care Unit (SICU); 5 South (a patient floor); Medical Intensive Care Unit (MICU); Hemodialysis; and the Outpatient Clinic.

Laboratory Services - This department performs analyses on specimens taken from patients. In a 9-month period ending June 30, 1989, the laboratory had conducted 41,097 venipunctures, 9,935 bacterial cultures, 4,730 blood cultures, 854 fungal cultures, and 815 tuberculosis cultures. The Laboratory consists of 4 areas: (1) Hematology, (2) Clinical chemistry, (3) Microbiology, and (4) Histopathology.

1) Hematology Laboratory - Hematology draws and analyzes blood samples from 50-60 patients daily. The technicians visit the patients to draw samples and then return to the laboratory to conduct the analyses. Cloth gowns are worn while blood is drawn and then replaced with a second cloth gown for lab work. All gowns are laundered for reuse.

Hematology generates two 30-gallon bags of infectious waste each day. It is rendered non-infectious via autoclaving and disposed of as general trash. Sharps (needles, broken glass) are placed in sharps containers and those containers are collected by housekeeping staff for weekly incineration.

2) Clinical Chemistry Laboratory - Clinical Chemistry conducts blood serum and urine analyses on samples drawn by the hematology technicians. Approximate waste generation rates for the principal disposables are:

- > Glass test tubes - 2,100 per week
- > Glass sample cups - 2,000 per week
- > Dry reagent slides - 21,000 per week

Like Hematology, Clinical Chemistry generates just under two 30-gallon bags of autoclaved waste each day. The laboratories are adjacent and share the same autoclave. The only disposable medical supply items that are reused are cuvette rings, used to test blood coagulation. Cuvette rings are washed and reused 5-10 times before disposal. This is done because of the high unit cost (\$2.30) of a cuvette ring.

3) Microbiology Laboratory - This section of the laboratory produces the greatest amount of discarded supplies by weight because most of its wastes are glass products. At least three 30-gallon bags of autoclaved waste are produced each day. The waste profile primarily consists of:

- > Petri dishes with Agar culture media - 1500 per week
- > Blood culture bottles and Contaminated Slides
- > Vitek Cards - 225 per week
- > Paper towels, gowns and disposable gloves (for tuberculosis isolation)

No disposables are reused. Petri dishes are not reused because they are difficult to clean properly and safely, and preparing media on-site is not cost effective.

4) Histopathology Laboratory - This laboratory is responsible for analyzing tissue specimens and body parts from surgery and the morgue. Histopathology produces no more than one 5-gallon bag of autoclaved waste per day. Pathological wastes are incinerated on-site. Disposable specimen containers containing formaldehyde are autoclaved and then incinerated on-site.

Surgery Department - The Surgery handles approximately 15 cases daily. According to DVA officials, DVA-Cin is one of the last hospitals in Cincinnati that continues to use woven gowns. The greatest volume of medical supplies disposed of after a single use are exam gloves and surgical sponges. Surgical sponges had been reused in the past, but are now disposed after a single use due to concerns over the AIDS virus. Surgery also utilizes operating room packs that are prepared with all the disposable products necessary for a specific type of operation. The packs are generally used in full, although sometimes specific items may not be used.

The Surgery Department generates between one and two 30-gallon bags of blood and body fluid waste per case, or 15-30 bags per day. Approximately 70 percent of this work is estimated to be contaminated paper waste. According to DVA-Cin officials, other Cincinnati hospitals generate three 30-gallon bags of waste per case; DVA-Cin maintains its lower waste generation rate through their continued use of wovens. Surgery carefully segregates wastes as they are generated. Wastes to be disposed of as blood and body fluid waste must be "grossly contaminated" (i.e., soaked, or dripping with blood). However, DVA-Cin feels that surgeons and nurses ought not be burdened by waste segregation duties during surgery, and are likely to curtail this activity.

Sharps are placed in sharps containers, which are then clear-bagged against leakage, and sent to the on-site incinerator. Blood and body fluid is taken by an infectious waste hauler for off-site treatment and disposal. All other waste is general trash.

Surgical Intensive Care Unit (SICU) - Almost all of SICU's eight beds are occupied on a regular basis. Cloth gowns are worn by patients and staff and are laundered for reuse. Procedure trays are re-sterilized on-site and reused, but SICU staff would like to go to the disposable packs like those used in surgery.

Blood and body fluid waste generated by SICU consists mainly of suction liners and tubes. Foley bags and chest tubes are flushed of their fluids and placed in general trash. I-V bags go directly into general trash. Sharps are boxed and incinerated on-site.

Waste is segregated into three categories: (1) sharps; (2) blood and body fluids, and; (3) general trash. Blood and body fluid wastes are strictly segregated into one-to-two 30-gallon bags per day. However, for those patients requiring isolation, SICU may generate as much as ten 5-gallon bags of medical waste per day for each patient. The number of patients in isolation varies.

5 South: Patient Floor - 5 South has 36 beds, of which 29-32 are occupied at any given time. 5 South provides pre- and post-operative care, including administration of medications and changing dressings. In total, the medical and surgical patient floors have 106 beds, of which 78 are occupied at any given time. Cloth gowns are generally worn on patient care floors, although disposable gowns are used whenever cloth is unavailable.

Waste is segregated into three categories: (1) sharps; (2) blood and body fluids, and; (3) general trash. 5 South generates one-to-two 30-gallon bags of blood and body fluid waste per day. In practice, nurses often dispose of non-blood and body fluid waste in the blood and body fluid waste container as a matter of convenience.

Medical Intensive Care Unit/Cardiac Care Unit (MICU/CCU) - the MICU/CCU has eight beds, all of which are constantly occupied. MICU/CCU reuses woven gowns and pressure bags. Pressure bags are used to introduce blood to a patient, and will be cleaned out for reuse.

Waste is segregated into three categories: (1) sharps; (2) blood and body fluids, and; (3) general trash. The assessment team again observed waste being dropped in blood and body fluid containers that did not need to be there; empty disposable urinals were observed in the blood and body fluid containers.

Hemodialysis - This unit has 9 treatment stations. Treatment occurs in shifts with a capacity to treat 55 patients each week. Treatment takes about 5 hours. Nearly all products are disposable, including aprons and masks. As is common practice in many hospitals, disposable dialyzers are re-sterilized and reused approximately 20 times before disposal. The practice of reusing disposables in health care is controversial and will be discussed further in this paper.

At least four 30-gallon bags of blood and body fluid waste are generated each day. Most of the disposable items are discarded in the blood and body fluid containers. Sharps are handled as previously indicated.

Outpatient Clinic - The clinic services approximately 500 patients each day. The services include: surgical procedures, medical exams, chemotherapy, dermatology, urology, plastic surgery, orthopedics, and ear, nose and throat. Plastic-coated paper gowns are worn for chemotherapy procedures (disposed of as cytotoxic waste) and often for other outpatient treatment and procedures. Reusable wovens would include sheets, pillow cases, towels and blankets. Badly soiled linens are often discarded rather than laundered. Gomco suction apparatus, suture removal sets and scalpels are all reused.

The Outpatient Clinic fills one 30-gallon bag of blood and body fluid waste each day. Chemotherapy wastes are packaged in white plastic containers, and eventually transported to final disposal off-site by a licensed cytotoxic waste hauler. Sharps are handled as previously indicated.

DVA-CIN WASTE GENERATION COMPARED TO OTHER HOSPITALS

As indicated earlier, DVA-Cin does not generate waste in the quantities common to hospitals having access to cost-plus-fee reimbursement mechanisms. On average, hospitals generate between 0.5 and 4 pounds of infectious waste per patient each day (3). The DVA-Cin facility produces approximately 0.6 pounds of infectious waste per patient each day, placing it at the low end of the spectrum.

There are inconsistencies in how hospitals from different States define what is infectious waste. For example, DVA-Cin classifies its laboratory waste as general trash after autoclaving, whereas a hospital in New Jersey would continue to list such waste as infectious, despite the autoclave treatment. Inflating the DVA-Cin's quantity of infectious waste to reflect lab wastes would raise the generation rate to 0.87 pounds per patient each day - still quite low in comparison to other hospitals. DVA-Cin's continued use of wovens is likely the primary reason for this lower rate.

POLLUTION PREVENTION OPPORTUNITIES AT HOSPITALS

The purpose of this section is to identify and evaluate the opportunities to minimize waste in a hospital setting. In addition to responding specifically to the waste profiles already presented, it is important to discuss issues affecting pollution prevention decision-making: the benefits/costs of disposable versus reusable products; the reprocessing of disposable items intended for single-use; the factors that continue to promote reliance on disposables; and the ability to implement better operating practices. The weight of State regulation also bears heavily upon this decision-making process, but is best addressed through the efforts of individual facilities formulating pollution prevention programs that comply with both legal and health requirements.

CHOOSING BETWEEN DISPOSABLE AND REUSABLE PRODUCTS

As stated earlier in this paper, there are four major factors supporting the medical professions preference for disposables: health and safety; cost; convenience; and space constraints. With the advance of technology, intricate devices are mass-produced and sold as single-use items, prepackaged and sterilized to relieve the hospitals of such quality assurance concerns. Labor and reprocessing costs are relieved, being replaced by the apparently lower costs of treatment, destruction, or disposal. Packs of disposable goods are custom-fitted, used and discarded, alleviating OR prep time and simplifying inventory control.

An excellent example of this decision-making process is found in the demise of hospital laundries. Reimbursement of medical services on a cost-plus basis provided the incentive to introduce new products and services to ease hospital workloads. This created a situation wherein funds were not allocated to upgrade traditional services, because there was little incentive to modernize operations and streamline procedures. In the case of hospital laundries, they were experiencing a rising demand for all linen products as inpatient services increased during this period. Antiquated laundry operations were incapable of meeting the new demand, becoming unable to efficiently process and sterilize the soiled linens. Acquiring disposable linens ensured an adequate supply of products, relieved an overburdened laundry, and provided cost savings by allowing hospitals to abandon or further downgrade this service, rather than invest in capital improvements. The cost-plus reimbursement method for medical services had led the hospitals into allowing formerly efficient laundries to lapse into a condition in which the most cost effective solution resulted in the greatest generation of solid waste (4). The assessment team for the VA-Cin Study suggested that the medical center's extraordinary use of linens and access to the Dayton laundry was a significant factor in explaining DVA-Cin's very low waste generation rate.

REUSING SINGLE-USE DEVICES

Hospitals and other health care facilities have attempted to reduce costs by reprocessing disposable, single-use devices/products (see Table 2 for a listing of the most commonly reused disposable products). Although the issue of reusing disposable devices is highly debated, health care professionals agree that if a product is to be reused it must be as functional, sterile, and safe as when new. In making this decision, health care professionals must consider the possibility of disease transmission or infection, assumption of product liability, decreased reliability, and cost.

These concerns impact the decision on what may be reused. The less critical an item, the more likely it can be reused (5). For example, because a bedpan is considered to be a non-critical item by the Center for Disease Control (CDC) and the risk of infection or disease transmission is minimal, reuse would be considered. However, an arterial embolectomy catheter would be considered critical and the potential risks from reuse great. The hospital will always opt for health and safety over any issue of economics or ecology.

TABLE 2 - DISPOSABLE MEDICAL DEVICES REPORTED TO BE REUSED⁶
(in Descending Order of Frequency)

Hemodialyzers	(46%)	Pacemakers	(1%)
Cardiovascular catheters and guidewires	(31%)	Pulmonary nebulizers	(1%)
Respiratory therapy breathing circuits	(18%)	Skin staplers	(1%)
Biopsy needles	(17%)	Urinary catheter plugs	(1%)
Cautery devices	(16%)	Allen needles	(<1%)
Anesthesia breathing circuits	(14%)	Arterial embolectomy catheters	(<1%)
Endotracheal tubes	(10%)	Condensing bottles	(<1%)
Suture stapie removers	(9%)	Operating room clamps	(<1%)
Syringes	(9%)	Ear syringes	(<1%)
Orthopedic appliances	(7%)	Face tents	(<1%)
Suction canisters	(7%)	Gastric pH monitors	(<1%)
Tracheal tubes	(6%)	Hypodermic needles	(<1%)
Bovie cords	(5%)	Javid tubes	(<1%)
Esophageal thermometers	(4%)	Oxygen masks	(<1%)
External pacemaker electrodes	(4%)	Microscalpels	(<1%)
Arterial catheter needles	(2%)	Stone baskets	(<1%)
Aseptic irrigating syringes	(2%)	Surgical gloves	(<1%)
Shunt connectors	(2%)	Triadaptors	(<1%)
Sterile skin scribes	(2%)	Tracheostomy tubes	(<1%)
Cholangiographic catheters	(1%)	Urethral stents	(<1%)
Esophageal stethoscopes	(1%)	Urinary bags	(<1%)

FACTORS AFFECTING CONTINUED RELIANCE ON DISPOSABLES

When considering reusable, or durable, products and reuse of disposable products as a means for reducing the rate of waste generation and its associated costs, infection control is the primary limiting factor. This paper has noted the increased attention that medical professionals are paying to this issue in the wake of public concern over the AIDS virus and other blood-borne pathogens. The CDC's Universal Precautions state that all blood and body substances must be treated as potentially infectious. As the first line of defense against pathogen transmissions, the medical community employs physical barriers to prevent contact with body substances: gloves, protective clothing, masks and eye protection. Single-use items intended for personnel protection provide hospitals with added assurance against accidental transmissions because they are used once, rendered non-infectious through autoclaving and either hauled off-site as general trash, or incinerated on-site. This eases the quality control burden for the hospital.

In any case, the barriers are employed but once, and that is what counts to the peace of mind of both doctor and patient. And, from a more pragmatic viewpoint, it is clear that, when considering the increasing frequency of AIDS in urban areas and the seriousness of all infectious diseases, health facilities must first ensure the sterility of a product or device, and then consider the opportunity for pollution prevention.

Another obstacle to converting from a single-use back to a durable product or device is that it may simply no longer exist in that form, or be too expensive to employ. The DVA-Cin procurement office indicated that disposable products had, in many instances, completely eliminated the market for the durable good. As a result, the durable version is either no longer available, or can be acquired through special-order supply companies that may be unable to guarantee long term availability and unable to provide sufficiently large quantities. This situation in turn drives up the cost of the durable version, potentially making it cost prohibitive.

POLLUTION PREVENTION OPPORTUNITIES AT DVA HOSPITAL

A variety of disposable devices ranging from syringes to hemodialyzers, from Petri dishes to bedpans, contribute to the growing waste streams generated by health care facilities. In order to successfully reduce waste, it is important for hospitals to reconsider the situations in which single-use devices/products are used and evaluate whether the disposable is still the best option. If reusable goods provide comparable reliability, sterility and safety, it would be reasonable to consider going back to the reusable. In those instances wherein the hospital is reprocessing single-use devices, it would appear that the durable version is an even more attractive substitute because the disposable has not relieved the hospital of the burden of re-sterilization, quality assurance, or labor costs.

Because of the diversity of the areas toured at DVA-Cin, it would be best to discuss pollution prevention opportunities by ward. The major disposable items in each ward will be reviewed.

Laboratory Services - Nearly all items used in Laboratory Services are disposable. All glass products (e.g., test tubes, sample cups, Petri dishes, slides, pipettes, pipette tips) are autoclaved and disposed after a single use as a matter of safety. Although glass could be re-processed for reuse, immediate treatment and disposal lessens handling time, decreasing the chance of exposure to accidents and spills. Plastic products (e.g., pipettes, pipette tips, test tubes, testing items, specimen bags, cuvette rings, etc.) are autoclaved and disposed after a single use. Of these, only cuvette rings are reused, due to their high cost. Since the only good durable substitutes would be made of glass, and glass would not be re-processed for the reasons given, substitution in this case would only increase the weight of the wastestream.

However, it was noted that the Microbiology Lab disposed of 1500 Petri dishes each week. Because they are glass, there is an opportunity to re-process the dishes and prepare them with new media. While they are difficult to clean, and Agar preparation is very labor intensive, it is important to consider developing an opportunity to have the dishes re-processed off-site. Such an alternative would allow the lab to continue functioning without the disruption from implementing inhouse reprocessing activities and significantly decrease the weight and volume of the waste generated by the lab. Within a two-mile radius of DVA-Cin there are eight other large hospitals (Holmes, Christ, Good Samaritan, Bethesda, Deaconess, and the University of Cincinnati hospitals, Children's Hospital Medical Center, and Shriner's Burns Institute). It would seem to be a reasonable entrepreneurial opportunity for some business to provide reprocessing services since it would have easy access to these main facilities. There are several more hospitals in the Greater Cincinnati area, but the ones listed are located in a way that facilitates the potential for a sharing of services.

Surgery - Because DVA-Cin already uses woven gowns, drapes, and instrument wraps, the greatest volume and weight of disposables in medical waste from surgery are made up of surgical sponges and exam gloves. While waste sponges should continue to be considered potentially infectious, it would be worthwhile to investigate whether sponges are being also used for purposes better suited for absorbent, reusable towels (i.e., cleanup activities). The CDC advises that all sharps, including syringes, be disposed rather than re-processed, and therefore this paper follows that recommendation.

The current use of wovens over disposables by DVA-Cin greatly reduces the potential volume of waste. Additional opportunity for substitution in this area is limited due to professional caution over health and safety, as well as cost considerations. It should be noted that the DVA laundry in Dayton does serve several facilities. As in the case of the Petri dish reprocessing recommendation, this may be an area in which several community hospitals may share a service and thus minimize their investment/capital costs.

SICU/MICU/CCU - The major disposable products used are catheters, tubing, suctioning equipment, I-V bags, needles and syringes. Catheters, tubing and suctioning equipment come into contact with body fluids during use and must be treated as potentially infectious. In accordance with Universal Precautions, needles and syringes are destroyed in a medical incinerator. However, I-V

bags never come into contact with body fluids and remain uncontaminated during use. Therefore, plastic I-V bottles could be safely reused for a single patient, and should be considered as a substitute for the I-V bags.

5 South - Patient Floors - Outpatient Clinic - The disposable products regularly used on the patient floors include suctioning equipment, tubing, catheters, blood transfusion equipment, chucks, and dressing supplies. Because of the inherent contact with blood and body fluids, these products are assumed to have a high risk of disease transmission. The only pollution prevention option recognized is in the use of chucks. Chucks act as linen and surface protectors, absorbing blood and body fluids in order that the reusable linens will not become grossly soiled and that surfaces will be easier and safer to clean. (Chucks are used in the laboratories as well to contain small spills at work stations.) Chucks are present throughout the hospital, and DVA-Cin may want to review the use of chucks to determine whether their availability has led to use in situations where they are not needed.

Hemodialysis - The major disposable products in this ward are I-V bags, tubing, gloves and dialyzers. Most of these items have been discussed, and it has been noted that the dialyzers are reused approximately 20 times before their disposal. The reuse of dialyzers has been found to be a common practice in health care institutions. An informal survey on the reuse of disposables, conducted at the 1984 Georgetown University International Conference, showed 46 percent of the respondents reporting the reuse of this item in their institutions (6).

With respect to high-tech items, it is believed that hemodialyzers are the only devices which have been studied in sufficient depth to show that function is not impaired through reuse (7). With this technical knowledge as evidence of safety and reliability, hospitals are able to write policies allowing dialyzer reuse as a waste reduction option.

ADDITIONAL OBSERVATIONS ON DVA-CIN'S POLLUTION PREVENTION EFFORTS

The DVA Hospital has already realized many of the waste reduction opportunities arising from product substitution and waste segregation practices. The hospital's standard use of wovens is a significant part of the reason DVA-Cin's waste generation rates are so low in comparison to industry average. The use of wovens in surgery accounts for the fact that DVA-Cin produces 50% to 65% of the waste normally produced during operations in Cincinnati area hospitals.

There has been some discussion on the reprocessing of glassware. The recycling of glassware from soda-lime (e.g., pasteur pipettes) may greatly reduce the volume and weight of a hospital's current wastes. However, a large percentage of the glassware used in laboratories is made of borosilicate which cannot be recycled with general consumer waste glass. Also, despite the reliability of disinfection from autoclaving there is a stigma ascribed to medical waste that may restrict or eliminate recycling as a pollution prevention option. Community recycling centers should be contacted regarding their policies for accepting waste glass from health care facilities.

The Outpatient Clinic uses both woven and plastic-coated paper gowns. For most treatments the woven gown is a safe, reliable barrier against infection and should be the primary gown worn by the Outpatient staff. The use of the paper gowns are best limited to those treatments, such as chemotherapy, which require more stringent infection control and increased personnel protection.

RESEARCH AND DEVELOPMENT OPPORTUNITIES

In addition to assisting in the identification of pollution prevention opportunities for health care facilities, a major concern for RREL in conducting these studies has been to look for those areas in which research and development may support advancing new alternatives. In learning of the concerns, difficulties and successes of the health care profession, RREL hopes to expand EPA's experience in the medical waste area and provide a solid basis for planning future research. Suggestions for further research in the health care industry are presented below:

Evaluate Reuse Potential in Single-Use Devices - As stated earlier in this paper, hemodialyzers are reused because they have been studied and evaluated closely to determine that such reuse does not impair their function, nor compromise patient safety. There are indications that other disposable products may not as yet have been studied in sufficient depth to make reliable determinations of their suitability for reuse. A cooperative effort could be established between EPA and representatives of the health care community to undertake this research and provide substantive data to either support or reject reuse considerations for the items listed in Table 2. Research data of this kind would give health care professionals a firm basis on which to make such decisions, as well as opening up a potential to uncover cleaner alternatives to some of the disposable products being reused.

Quality Assurance - There are also legal and ethical considerations associated with the reuse of disposables. Among which are the manufacturers disclaimers of warranty for reuse. There is agreement that manufacturers can offer a higher assurance of sterility than an individual health care facility. Research conducted by the EPA in cooperation with health care professionals, other Federal agencies (such as the Food and Drug Administration), and trade associations can form the basis for developing a protocol for reuse, giving hospitals a standard under which to set down operating procedures and institutional policies.

Hidden Cost Factors - There appears to be some confusion in comparing the relative costs of disposables versus reusables. The unit cost of a disposable does not represent the full cost of actually using that product. Disposal costs are becoming an ever more important factor as landfill and incineration regulations become increasingly more stringent. For its part, the reusable also carries storage and handling costs. The EPA may wish to conduct analytical studies in conjunction with health care facilities in order to quantify these costs as an aid in decision making.

Development of Reprocessing Capacity - Two pollution prevention alternatives cited by this paper involved reprocessing services that have been diminished by the disposable revolution. Space and labor constraints, coupled with the general availability and convenience of disposables, appear to be the major obstacles to on-site reprocessing of durable materials. However, as health care cost containment gains increasing importance, reprocessing may become cost effective for some items. The potential for promoting some reprocessing capability should be explored, particularly in those areas exhibiting a high density of medical facilities.

Developing a Reusable Market - Certain bills in Congress to amend the Resource Conservation and Recovery Act (RCRA) will require that Federal agencies meet certain objectives for use of recyclable products. The EPA and DVA should consider working together in developing procurement guidelines for the DVA which will stimulate the production and distribution of reusable and recyclable products.

CONCLUSION

In the case of the DVA study, the Assessment Team was impressed by the difficult challenges undertaken by the hospital professionals to perform their duties of human care while attempting to minimize the impact of those activities on the environment. Follow-on discussions indicate that this is a dynamic process for DVA-Cin, as they develop initiatives in training, information sharing and cooperation with other Federal agencies.

For its part, the EPA hopes to learn from future cooperation with DVA, seeking the health care professionals' advice and guidance in planning and implementing research programs to respond to the needs of the medical community in the areas of hazardous waste, infectious waste, and other waste-streams. Opportunities to reduce these wastes do exist, and additional opportunities will be uncovered through research. Research will also provide the data on which to make operational decisions of benefit to health care facilities, while favoring environmental considerations.

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- 4) "Reusable Linens: An Economical Alternative to Disposables", Hospital Material Management Quarterly, February 1984, pp. 7-26.
- 5) According to the Center for Disease Control, a critical item is one that will enter the vascular system or any sterile area of the body. An item is semi-critical if it comes into contact with only intact mucous membranes. A non-critical item comes into contact only with intact skin.
- 6) "Reuse of Disposable Medical Devices in the 1980s", Proceedings of the International Conference. Institute for Health Policy Analysis, Georgetown University Medical Center, 1984, Appendix B.
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A TEN YEAR REVIEW OF PLASTICS RECYCLING

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ABSTRACT

A short history of the practice of plastics recycling as practiced in the United States and Europe for the past ten years indicates that much progress has been made in educating the public sector about the environmental damage done by indiscriminate disposal of plastic items. Recent legislation has made the collection of some discarded plastic items more efficient, and has provided economic incentives to recover and reuse waste plastics. The methods of collection, separation, cleaning, and fabrication of plastic wastes into useful and saleable items are discussed. Also discussed will be examples of products made from recycled plastic.

INTRODUCTION

Considering the enormous quantities of plastic material produced in this country, as shown in Figure 1, it is little wonder that discarded plastics have become a significant portion of municipal waste streams. Figure 2 shows the composition of municipal waste in the United States; the quantities given are percent by weight, for while plastics constitute only 6.5% (the General Accounting Office estimates 7.2%) by weight, the inherent low densities of the resins and low bulk densities of plastic products such as bottles are said by some to compose 32% of the volume of landfilled waste. A large part of the waste is discarded packaging of one type or another. The low price of plastic shrink wrap, blister packs, bottles, and infinitum, has resulted in a throwaway mentality; we discard items which appear to have an almost infinite life if landfilled, and sometimes present a hazard to marine life. Incineration is an option for most plastics, which with the exception of some of the halocarbons, have a high fuel value; incineration recovers only a part of the energy content of the materials since the energy consumed in resin manufacture is wasted. Modern plastic materials are almost universally derived from petroleum. Recovering and recycling plastics means that in addition to the hydrocarbon content saved, a large part of the energy expended in production is also saved.

A common perception is that plastics are a relatively recent invention. In reality, the first synthetic plastic, Celluloid, was developed over 120 years ago (1869), and Bakelite over 80 years ago, in 1909. The volumes of these and subsequently developed plastic materials such as cellulose acetate and poly(vinylchloride) (PVC) were relatively small, and since they were made into semidurable items such as electrical equipment or insulation, motion picture film, etc., they were not considered a nuisance when discarded. The "Plastics Age" might be considered as beginning in the late 1940's when the high volume production of low density polyethylene (LDPE) began. The rapid growth of the industry is illustrated in Figure 1, which includes all plastics, thermosetting (once formed or molded they cannot be reshaped by heat), and thermoplastics (which within reason can be recycled by remelting, and reshaped into different objects). Production volumes of the more common thermoplastics are shown in Figure 3, along with the amounts of the four major types recycled in 1988.

This review will primarily be concerned with thermoplastics, particularly those most often fabricated into disposable items which have a very short usable life and are discarded shortly after purchase. The sources of wastes, means of recovery from waste streams, technologies for converting the waste material, and uses and markets for the recycled plastics will be discussed.

TYPES OF THERMOPLASTICS

Thermoplastics are generally divided into two groups. The first group, often called commodity plastics, would include the polyethylenes (PE), polypropylene (PP), poly(vinylchloride) (PVC), polystyrene (PS),

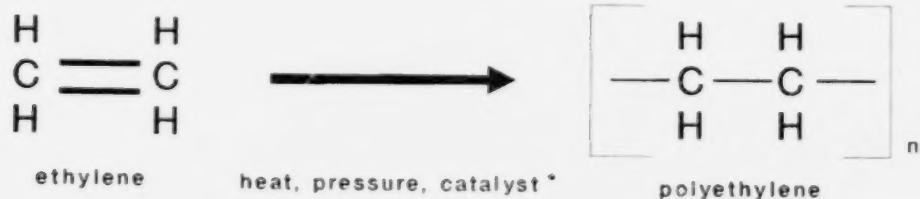
their copolymers, and poly(ethyleneterephthalate) (PET). These products are low priced and produced in huge quantities; prices range from \$0.50 to \$0.70 per pound. The combination of low price and physical properties explains their widespread use in disposable packaging, in one-time use agricultural and architectural coverings, and in some engineering applications where their physical properties are acceptable.

The second group is called engineering plastics. Characterized by higher strength, resistance to heat, and impact resistance, they have become widely used to replace metals in many automotive, appliance, aerospace, and industrial products. Prices of these range from \$0.85 to more than \$10.00 per pound. Their applications to more durable goods and lower production volumes result in less of a pollution problem and will not be discussed at length in this review. An exception is PET, which has excellent clarity, mechanical properties, and heat resistance. PET could be said to straddle the line between commodity and engineering plastics, as it is the plastic used in the ubiquitous clear plastic soft drink bottles, some hot filled food products, and in many mechanical applications as well. PET can also be made into fiber (Dacron, Kodel, etc.) and films (Mylar, Cronar).

RESIN MANUFACTURE

The great majority of modern synthetic plastics are derived from petroleum or natural gas. Polyethylenes and polypropylene belong to a class called polyolefins, since their starting materials (monomers) are olefins made by thermally cracking the larger hydrocarbon molecules in natural gas liquids or petroleum fractions. Poly(vinylchloride) (PVC) might also be described as an olefinic material, since it differs from polyethylene only by having every second hydrogen on the chain replaced by an atom of chlorine. Generalized structures of the polyolefins and PVC are shown below.

POLYETHYLENE



* Low density polyethylene (LDPE) is produced by contacting ethylene monomer and an organic peroxide catalyst (or more properly, initiator) at pressures of 15,000 to 50,000 psi and temperatures of 300° to 575°F.

POLYPROPYLENE



** Polypropylene is polymerized with Ziegler-Natta type catalysts similar to those used for high density polyethylene but at lower temperatures and pressures.

POLY(VINYLCHLORIDE)



*** Poly(vinylchloride) polymerizations are carried out with peroxides, persulfates, or redox catalysts at relatively low temperatures and pressures. The type of catalyst and method of polymerization vary according to the intended end use for the product.

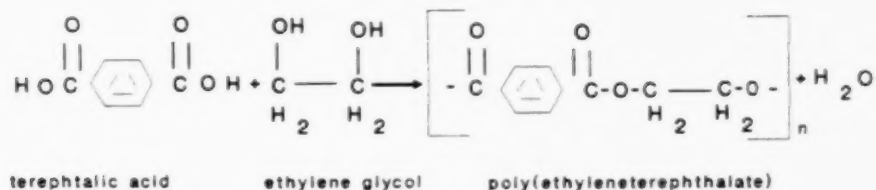
(C = carbon, H = hydrogen, Cl = chlorine)

The polyethylenes can be thermally cracked or depolymerized back to lower molecular weight polymers, or under severe conditions, to oily materials or to carbon and hydrogen. This process has been proposed as a method of recycling but will not be discussed here. PVC can also be thermally cracked, with the evolution of hydrogen chloride gas (HCl), which is poisonous and corrosive. In common with other organic polymers, they can also be depolymerized or otherwise affected by the ultraviolet portion of sunlight and oxygen in the air. This is a slow process, and is made even slower by special inhibitors (antioxidants and ultraviolet stabilizers) added before fabrication into the final product. Without these inhibitors many uses for plastics (such as telephone cable jacketing exposed to sunlight and heat) would be limited.

High density polyethylene is catalyzed by heterogeneous catalysts which are organometals such as triethyl aluminum combined with titanium tetrachloride at 180°-250°F and 150-200psi.

POLY(ETHYLENETEREPHTHALATE)

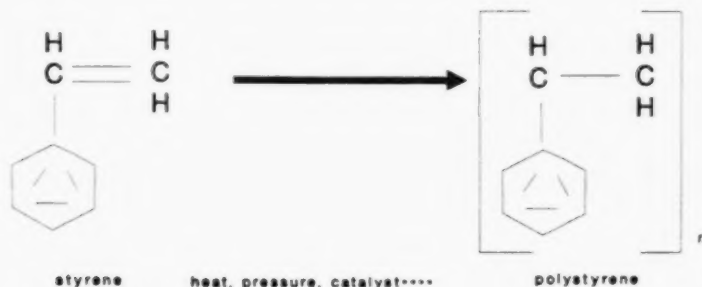
PET is also a petroleum derived product; a copolymer of terephthalic acid, (which is made by oxidizing para xylene), and ethylene glycol, or other glycols such as diethylene glycol or cyclohexane diethanol. A simplified reaction sequence showing the direct esterification reaction (there are actually three different processes all arriving at the same end product) is shown here:



The fibers Dacron, Kodel, etc., made from PET are chemically identical to the resin made into bottles. Some attempts to incorporate them into the recycling chain will be covered in a later section.

POLYSTYRENE

General purpose polystyrene is a clear, somewhat brittle resin. Most disposable polystyrene items are of resins made by the following reaction sequence:



**** A peroxide such as benzoyl peroxide.

The familiar foamed beverage cups, insulated containers, and home insulation are chemically identical to the clear drinking cups used on airlines. The foamed materials are made by incorporating a hydrocarbon such as n-pentane during the polymerization process.

SOURCES OF PLASTICS WASTE

DOMESTIC

As indicated in Figure 2, in 1984 the percentage of plastics in municipal trash was about 7.2% by weight, or about 9 million tons - almost

double that present in 1976. By volume, plastics amount to about 32%, according to Ramani Narayan of Purdue University (1). No assay of the volumes of individual polymers (PET, PE, PVC, etc.) appears to be entirely accurate, but it seems fair to assume that overall, the ratios of the plastics made to disposable items such as bottles, packaging films and containers, etc. would approximate the ratios of resins sold for these purposes. In 1988, over 16 billion pounds of plastics were used in packaging. This excludes the 935 million pounds of PET (polyethylene terephthalate) sold for soft drink and specialty bottles (2).

AGRICULTURAL

The main uses of plastics in agriculture are in mulch films, feed bags, fertilizer bags, and in temporary tarpaulin-like uses such as covers for hay, silage, etc. A growing use is temporary covering for fields that are being fumigated. This film and the various bags would appear to be prime candidates for recycling, as they are reasonably clean and easily accumulated. Mulch and covering film are usually discarded after they have begun to deteriorate, generally as the result of being exposed to sunlight. Reprocessed resins produced with a high proportion of these films will have poor physical properties.

INDUSTRIAL

Industrial and construction use of disposable plastics is difficult to quantify as some plastic film is used for temporary enclosures and then left in place as a vapor barrier, while some is removed and discarded. Polystyrene foam is likewise widely used as insulation, with an almost indefinite lifetime, but many industrial products are shipped with foamed "popcorn" or molded packing, almost all of which is discarded. The low densities of these foams (1-2 lbs/ft³ vs. soil at 70) make them especially undesirable in landfills, while at the same time making hauling costs to recyclers prohibitively high. Much machinery, lumber, plywood, bagged goods such as cement and mortar are shipped with polyethylene film covers. The majority of this could be easily recycled. Shrink wrapped cases are replacing corrugated paper cartons in many grocery items. Groceries should be prime candidates to initiate recycling programs, since they could serve as collection centers as well as being generators themselves.

"FAST FOOD" CONTAINERS

Foamed polystyrene is widely used in food packaging (meat and produce trays) at the retail grocery level, but the largest part of this 725 million lb/yr market is in "fast food" containers. The volume of waste generated from this 725 million pounds is tremendous, for the density of the foamed material is only 2 to 3 pounds per cubic foot, which would indicate an uncompressed bulk of 13 to 20 million cubic yards occupying space in our landfills. A consortium of chemical and oil companies has announced the formation of the National Polystyrene Recycling Company to build five regional plants to recycle polystyrene (3). The five plants, said to cost \$14 million, plan to collect the used material from restaurants, hospitals, schools, and other big users in 30 states. The

consortium is only planning to recycle 25% of the scrap available; there is obviously room for others to enter the market, though finding large, easy to collect volumes of scrap may be difficult.

MILITARY

No reliable estimate of the amounts of recyclable plastics used by domestic military installations is presently available. Contact is now being made with the Department of Defense to quantify their usage. Because of the concentration of these facilities, recycling should be easier than for domestic waste.

AUTOMOBILE WRECKING

The amount of plastics used in automobile manufacturing has been growing at approximately a 9% rate over the past ten years. Even in 1979 (the approximate date of production of autos now being scrapped) the amount of plastics used in automobiles was 787,000 tons (4). It would thus appear that a large part of this could be recovered. An investigation of this was done in 1975 by the Bureau of Mines (5), but only a crude sink/float technique was used to separate the plastics fraction, and little interest was generated since good homogenous materials could not be produced. Interest is growing in identifying the various plastics components in automobiles with a molded or stamped-in label so that salvagers could more easily segregate the types as they strip the vehicle prior to crushing and grinding. An evaluation of an innovative process to separate the various kinds of resins from finely ground waste, such as from automobile grindings is planned as a joint project between EPA and a large plastic producer.

WIRE AND CABLE

A large source of recyclable plastic should be the electrical and telephone cables from demolished buildings. Until recently, these were burned to recover the copper or aluminum; now that strict emissions controls are required on these incinerators, physical separation of the plastic insulation would appear to be a viable option. One site where wire and cable was processed to recover the metal conductors is reputed to have over 100,000 tons of mixed plastic "fluff" in a pile covering over 7 acres. The amount of plastic recoverable from wire and cable is not known, but 433 million lbs. of PVC, 386 million lbs. of LDPE, and 125 million lbs. of HDPE were sold for insulation in 1988.

COLLECTION/RECOVERY

Segregation and collection of waste plastics from agricultural operations, industrial, and construction sites should not be difficult if it were economically attractive to the generator. These operations typically generate relatively large quantities of discarded plastics in small areas, so segregation would appear to be entirely feasible.

DOMESTIC WASTE

A successful plastics recycling operation must have a dependable source of waste which is not overly contaminated with wet garbage, which makes sorting and washing difficult. The recycling plant should not be too far from the collection points, since the cost of hauling the bulky materials such as empty bottles or polystyrene foam would greatly increase operating costs. An efficient collection system is therefore mandatory, and should operate over a large enough area (preferably urban) to supply an adequate amount of feedstock. Thus the collection of reprocessible plastics from urban waste has proven to be the most difficult and costly aspect of polymer recycling. In the United States, early attempts to hand sort municipal garbage in bulk by spreading it over a moving conveyor belt proved to be unsuccessful, mainly due to the difficulty of finding employees willing to perform the sorting for low wages. The present trend is for states and municipalities to enact legislation requiring homeowners, and in some instances businesses, to presort trash. Under this system, separate containers are furnished for wet garbage, newspapers, glass, metals, and plastics. Several states, Michigan among them, have enacted "bottle laws" which require purchasers to pay a deposit on all beverage containers, whether or not they were meant to be returnable. This has resulted in greatly increased recycling of PET bottles; but other types of containers such as PE milk and detergent containers, bags, film, etc., have been relatively unaffected although these items constitute about 80% of all plastics trash. The City of Cincinnati recently started a voluntary recycling system, and has found that 65% of households are participating; they had only predicted 35%. It is apparent that the public is aware of the need to recycle. In Cincinnati, the only plastics that the recycler, BFI, will take are PET bottles, (easily identifiable, being clear, usually with an opaque base cemented to them), and polyethylene milk bottles, which are mostly translucent white. In mixed wastes, these would be worth the extra effort to separate, as they can be easily hand sorted from a conveyor belt. In Europe, PVC bottles are widely used for wine and edible oils, and some attempts have been made to separate them for recycling. PVC bottles are usually clear, and differentiating them from PET might be difficult for an untrained person.

As mentioned previously, a special case which is well worth mentioning are the foamed polystyrene fast food trays and cups which have become a litter problem, as well as occupying a disproportionate amount of landfill volume. Resin producers have formed at least two joint ventures to recycle these discards into usable products (3).

In contrast to American practice, the separation and collection of recyclables in Europe is much more efficient and has a long history. Kunststoffe German Plastics, a technical magazine which covers the production, testing, and fabrication of plastics, devoted a large part of its May 1978, issue to plastics recycling (7). Since Kunststoffe is aimed primarily at the production and fabrication of plastics, the means used to

collect and separate plastics are not covered in detail. The articles covered in this issue discussed other aspects which will be covered later in this review.

SEPARATION TECHNOLOGIES

MUNICIPAL WASTE

Municipal waste from which the "wet garbage" has been separated is the feed to several recycling operations in European countries. A flow chart of a Dutch process which had been operating for a year in 1978, is shown in Figure 4 (8). The TNO system operates at 15-20 tonnes (33,000-44,000 lbs) per hour, and is designed to recover metals, plastics, and papers from a mixed waste stream using a number of different operations. Figure 5 is a Sankey diagram of the TNO process, indicating the percent recovery of the various input materials. It is apparent from the flow chart that resorting to mechanical means to separate the various fractions is very difficult; one can count fourteen major pieces of capital equipment, exclusive of the conveyers, etc. required to carry material from one operation to the next. The final product is merely called "bales of plastic", apparently a mixture of all the overhead from the zigzag air classifier.

A process developed by SINTEF in Norway (9) is shown in Figure 6. Note the similarities to the TNO process as far as the types of equipment employed in the first stages. Both preshred or grind the refuse, use trommels to screen it, then zigzag air classifiers to separate the light from the heavy fractions. The SINTEF process takes the overhead from the air classifier and passes it to a simple wash tank holding 250 liters (66 gal.) of water where it is washed and separated into sink/float fractions. In reality, this separation is relatively easy; after the ground particles of plastic are freed of dirt, oil, grease and adhering paper, the polyolefins (density <1) will float, while the PVC, other plastics, and wet paper, etc. whose densities are greater than water, will sink. While the polyolefins all have a density less than one, and will be separated as a mixture of HDPE, LDPE and PP, using the mixture to make even as prosaic as a garbage bag is difficult. This problem will be covered in a later section.

Even if plastic waste has been presorted at the curb, some final classification is usually done to segregate the more valuable plastics from the main stream. One such system is described in a paper recently presented at Recyclingplas IV (10). The AKW plastics recycling plant which has been operational in Blumenrod, West Germany since July 1988, is said to have its entire output sold. The Blumenrod plant, in the Coburg district, collects waste from a population center of about 280,000 people. Three collection systems are employed in the district. One, (Figure 7-1) has a number of larger receptacles located in heavily used areas such as near parks, city centers, etc. The receptacles are marked for glass and for paper, with the non recyclable material segregated. Further separation must be done in a "Material Recovery Facility" (MRF). The amount of material collected from these points, while appreciable, is not nearly

enough to justify the construction of a recycling facility, so a second system of curbside collection is also practiced (Figure 7-2). Here the recyclables are all placed in a single bin which is taken to the MRF. This system, which is presently used in several U.S. cities and proposed for others, requires the householder to separate the waste paper, metal, and plastic into a "green bin", which greatly facilitates the sorting at the recovery facility. This system does not require the householder to make the decision as to what constitutes the most desirable recyclables, but does greatly decrease the amount of final sorting required. The third, and preferred system, requires some education of the householder, as a three bin system is in place, is shown at the bottom of Figure 7. In all three cases a final sorting is performed at the recycling plant.

Diagrams of some of the early recycling operations indicate that little or no presorting was done. Even if the sink/float separation mentioned in the previous paragraph were used on a granular waste plastic stream containing say, polyethylenes, polypropylene, foamed polystyrene, solid polystyrene, PVC, and PET, the polyethylenes and polypropylene (polyolefins) plus a large portion of the foamed polystyrene would float. Attempts to fabricate useful items from this mixture would probably be futile, since the polyolefins and polystyrene are incompatible. The bottoms would have a mixture of all the others, and attempts to fabricate useable products from them would also yield articles of both poor strength and appearance.

It is apparent that an efficient recovery operation must segregate the various types of plastics either by hand sorting before grinding, or by some mechanical means. Figure 9 is a pictorial presentation of the AKW sorting plant where mixed waste is hand sorted on moving conveyers before grinding. Although some attempt has apparently been made to presort at the collection points, metals, cardboard, paper, wood, and plastics are hand sorted again. In this illustration, only two classes of plastics are defined, rigid and film, although the text of Reference 10 uses the terms plastic film and plastic bottle material. Since 99+% of plastic films are polyolefin, no problem would likely result from compounding them into items for resale if an intensive mixer were used. Figure 9 does not indicate it, but the plastic bottles should be further separated into three groups, since not only are the three major types incompatible, but they represent products of higher economic value if they are recovered in a relatively pure form.

Of particular interest to most American recyclers are PET bottles, as they are easily identifiable, being clear, usually with an opaque base cemented to them, while polyethylene bottles are mostly translucent white. Both of these are worth the extra effort to separate, as they can be easily hand sorted from a conveyer belt. In Europe, PVC bottles are widely used for wine and edible oils, and some attempts have been made to separate them for recycling. PVC bottles are usually clear, and differentiating them from PET might be difficult.

After separation or sorting, the plastic fractions are finely ground or shredded (in the earlier TNO and SINTEF processes the total stream was ground then separated in an air classifier) this would appear to be a relatively straightforward operation, but in practice can be very difficult. Plastics are tough, and tend to tear rather than break cleanly. Also, when grinding a waste stream, there are pieces varying in size from one inch (25.4 mm) to pieces several yards or meters long; thicknesses may be as little as 0.001 in. (0.0254 mm) or up to 0.5 in. (12.7 mm) this variability requires grinding equipment with extremely close tolerances, and the presence of dirt, grit, or other contaminants causes these to change quickly. Grinding also results in heat buildup which can change knife clearances, and make the plastic more resilient and harder to cut cleanly. Some grinders operate with a gas stream flowing through the grinding chamber (some specialized operations use liquid nitrogen) which serves the dual purpose of cooling and conveying the material. The AKW system grinds the waste under water, which cools more efficiently and aids in washing the plastic particles.

MECHANICAL SEPARATION/CLASSIFICATION

Zig zag or cyclone air separators used in the earlier European processes are not very efficient for classifying particles of low density with high surface to volume ratios such as granulated plastics. This, coupled with the small density differences between the several types of plastics (approximately 0.9 to 1.5gm./ml) yield an overhead product that is a mixture of the feed material. The AKW process uses hydroclones, which are cyclones operating with liquids as the conveying media, as shown in Figure 8. The hydroclones complete the washing, and separate the solids into a heavy fraction which in their operation is primarily PVC and PS (polystyrene), and a light fraction composed of the polyolefins (low and high density PE and PP). These fractions are then dewatered in a centrifuge and dried, both operations being carried out in conventional commercially available equipment. An overall view of the AKW MRF is shown in Figure 9.

PET BOTTLES

Another special case in the municipal waste classification is the ubiquitous PET soft drink bottle. In 1979, 1.5 billion of these containers were produced, consuming about 150 million lbs. of resin (11). PET is now used in many other types of containers, from salad oil to peanut butter; the 1989 usage is expected to be 1.02 billion lbs. These bottles are easily identified in waste (and often as roadside litter), and the recycled resin has a high resale value. These facts have resulted in PET becoming the most profitable of plastics recycling efforts, aided by mandatory recycling laws such as the one in Michigan. Another incentive is offered by machines which return cash for each bottle inserted; the machines grind the bottles for periodic collection by the recycler.

Most PET bottles have two piece bodies, the clear or slightly tinted bottle proper, and a base molded of high density polyethylene. The caps and seal rings (which stay on the body after opening) are aluminum with an ethylene-vinyl acetate gasket or liner. Earlier bottles had a glued on paper label, which are now being superseded by shrunk on polyethylene film labels. Several recyclers have been in operation since 1980. Most of them grind the bottles, air separate the paper and fines, then use a sink/float process in water to separate the PE base from the PET and aluminum. The Center for Plastics Recycling Research (CPRR), has a pilot plant in Piscataway, NJ which uses an electrostatic separator to remove aluminum after the above separation steps (12). CPRR is offering the process for license at a nominal cost.

PRODUCT FINISHING

Although some plastics fabricators have equipment capable of extruding or molding articles from the fluffy granulates, the majority are used to handling pelletized resins. It is therefore preferable to pass the dried granulate to an extruder to melt blend or homogenize the mixed plastics and to form small pellets which are much more easily fed to the final fabrication step. Plastics extruders are deceptively simple in appearance and operation, consisting of a heated cylinder enclosing a long auger like screw. The screw is specially configured for each type of plastic, and sometimes has special mixing flights, interruptions for the removal of volatiles from the plastic melt, etc. The design of extruders and their ancillary equipment is a complex mixture of art and science, and they must be chosen with great care.

Extruders used to blend and pelletize the granulate are usually fitted with a "crammer feeder", which is an auger to force the fluffy granulate into the feed section of the extruder proper. As the mixed plastic particles are forced through the heated cylinder, they are heated both by conducted heat from the cylinder, and by friction as they are compressed by decreasing the depth of the screw flights. The frictional heat is of such magnitude that most extruders only use external heat for startup; while running they must be cooled by air or water on the external barrel surface, and water into the center of the screw. Feedstocks such as the granulated mixed plastics wastes often have some water or other volatiles in them despite the predrying step, and may require devolatilization in the extruder. This is accomplished by decompressing the melt near the middle of the barrel length, where a vacuum is applied. The melt is then further homogenized, passed through a fine screen, and exits the extruder through a multi holed die, where it is cooled, solidified, and chopped into pellets.

Much emphasis has been placed on homogenizing the molten plastic at this stage of the operation. Non crystalline polymers of similar chemical structures can often be easily melt blended and molded or extruded into useful products of reasonably high quality. PET is an excellent example; it is routinely recycled into molded products or carpet fibers. Mixtures of crystalline polymers such as the polyolefins are much more difficult to homogenize, since each of the three components has a different melting

point (low density polyethylene 110° C., high density 120°, and polypropylene 140° C.). When such a mixture is melted by merely raising the temperature without intensive mixing, the crystallites or spherulites of each specie are not broken up, with the result that a thin film or fiber will have small particles (gels) of polymer or dissimilar polymers such as PVC, oxidized materials, etc. visible to the naked eye. Such impurities sometimes act as stress risers, weakening the product, and at the least are unsightly. It is therefore extremely important that a good homogenous blend of any recycled product be made at the recycling plant. Many good homogenizing extruders are commercially available, and while not able to make virgin quality product from scrap, will still make good recycled material.

To this point, only regrinding and pelletizing in preparation for reprocessing has been considered. Another possibility for recycle exists, which is to depolymerize the resins back to their monomers and either remake them into polymers, or find other uses for the molecular fragments,^{13, 14, 15} some of which may not be polymerizable. Polyolefins may be thermally depolymerized or "cracked", yielding a mixture of liquid and gaseous products. The latter will usually consist of the original monomer (ethylene, propylene, etc.); but most of the mixture will be composed of many higher olefins unless extremely severe conditions are used. Halogen containing polymers such as PVC will evolve hydrogen chloride (HCl) when heated, become brittle, and finally insoluble. Polyesters such as PET are easily depolymerized by hydrolysis in glycols or even water at high temperatures and appropriate pressures. Eastman Chemical Products Inc. has demonstrated that they may be depolymerized in propylene glycol (16), then reacted with acids such as maleic to produce a thermoset polyester resin. Goodyear and duPont are also doing research using the depolymerization approach.

APPLICATIONS FOR RECYCLED PLASTICS

Pending development of better means of sorting the various types of plastic materials into relatively pure fractions, it appears that at the present only two types could be considered for making into high quality objects, PET and HDPE. High density polyethylene (HDPE), from such objects as discarded milk containers, can be easily distinguished from other components of a waste stream, or sorted at the curb. After the bottles are reground and cleaned they may be recompounded into pellets for remolding or extrusion. The cost of such recompounded material is 25-35% less than virgin resin, and if strict quality control is performed by the recompounder, physical properties may be in the same range as the virgin polymer. It would seem that several non appearance automotive items could be made from reprocessed material, such as windshield washer fluid containers, fender and trunk liners, etc. Procter and Gamble has pioneered among consumer goods companies in the development of recycled plastics packaging. Recycled HDPE is used to make test quantities of one gallon jugs for Cheer[®] detergent. These containers are made in a three layer

extrusion; virgin resin is used for the outer appearance layer, reclaim for the center, and again a layer of virgin for the inside in contact with the product.

Polyethylene terephthalate (PET) is already being recovered in such purity that it is suitable for some fiber uses such as pillow or cushion fillers. Procter and Gamble has tested clear PET bottles for Spic and Span^R Pine cleaner. There are a number of automotive or industrial parts which could be made of reprocessed PET, either clear (radiator overflow tanks) glass filled (filler caps, terminal blocks) or compounded with other resins such as low density polyethylene (LDPE) which improves processibility, lowers moisture absorption, and also elevates some mechanical properties. (LDPE/PET blends have lower moisture absorption than PET alone).

Most lead-acid automobile batteries are contained in polypropylene (PP) cases. Cases from batteries being reclaimed for their metal value are ground to 1/8" pieces, washed, mixed with a foaming agent, and extruded into I beams for bed rails (17). To quote from this article in Modern Plastics "One rather curious factor emanating from this reclamation project is a morphological change in the scrap PP which is thought to stem from the residual lead and sulfur imparted by the battery environment. The precise nature of the chemistry has not been determined, but the result is definite improvements in such properties as impact strength, flexural modulus, and heat deflection." The above phenomena might also be related to results reported by Zamorsky and Muras (20) when PP was repeatedly extruded and the melt viscosity only decreased by 4.4%, while the carbonyl index during weathering was relatively unchanged.

The example of the reclaimed PP given above is unusual, for reclaimed materials usually have physical properties inferior to virgin resin. Nearly all molders of products such as battery cases will use resins of about the same molecular weight and molecular structure. When recompounded, these polymers will retain essentially the same structure, so they will be physically compatible, and retain most of their original properties. Clear plastic materials picked from domestic trash on the other hand, will appear to be uniform, but in reality the many manufactured items will be made from a variety of resins having vastly different molecular weights, copolymers (such as ethylene-vinyl acetate), pigments, and other additives. Despite thorough washing in systems such as the AKW process mentioned above, some of the products were used to package motor oil, vegetable shortening, or other products which absorb into the polymeric matrix and change its properties. This sensitivity to contamination is much more evident in crystalline polymers, a class which includes the polyolefins (polyethylene, polypropylene, etc.).

Assuming that the reclamation process is efficient enough to separate plastics from the other constituents in a waste stream, and that further, these are separated by some mechanical method which yields two streams, one having a density of less than 1.0, the other above 1.0, a number of marketable items could be produced. A few such items and sources of raw materials are shown in Table 1.

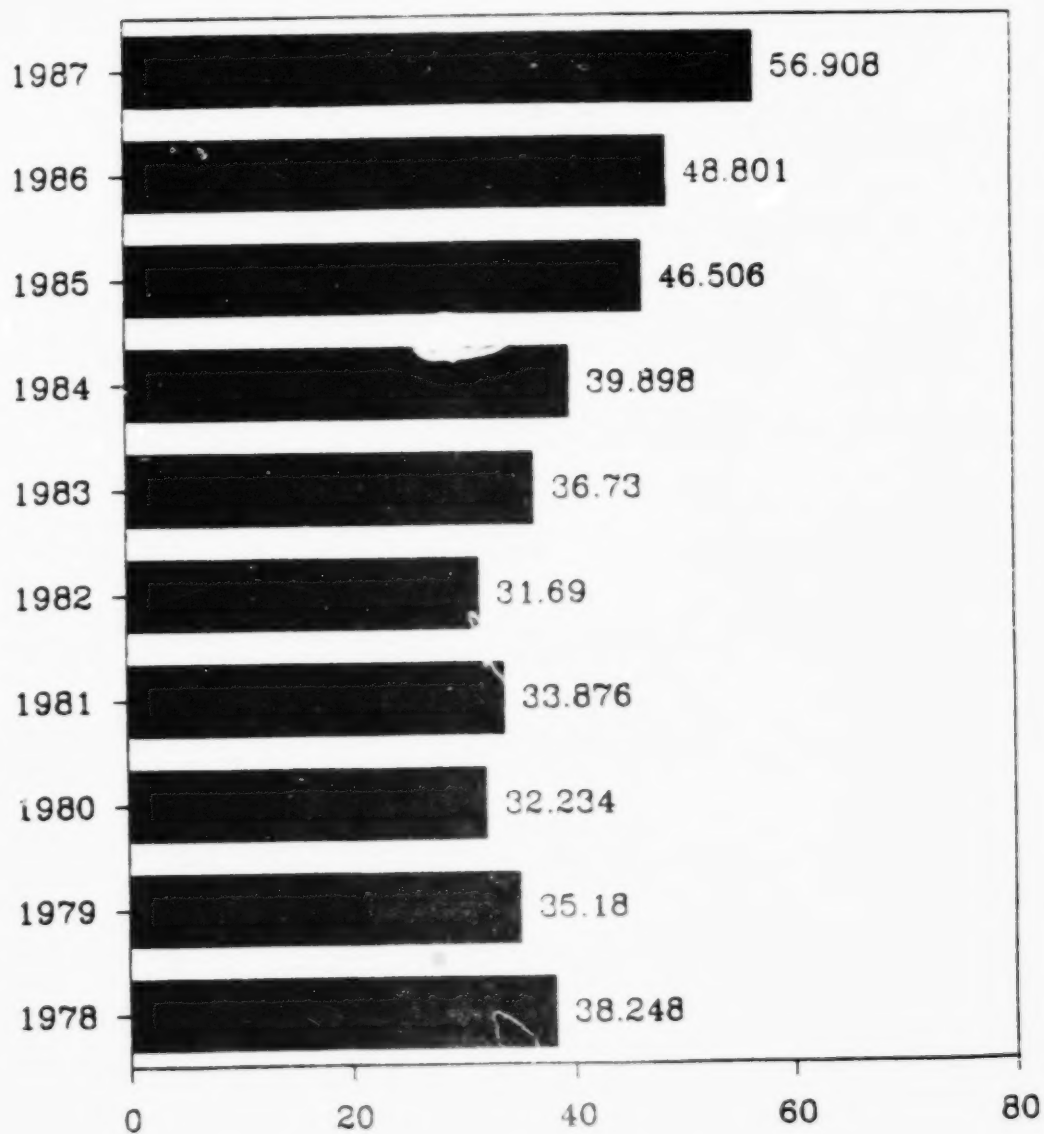
CONCLUSIONS

The continued buildup of plastic wastes in landfills has become a major source of concern for many sectors of society. Plastics manufacturers and their trade organizations have begun to realize that they must help diminish the problem, and turn their considerable technical skills to this end. Cooperation between these organizations, academia, and EPA has been excellent, and together, the amount of plastics recycled should be greatly increased.

TABLE 1
PRODUCTS MADE FROM RECYCLED PLASTICS

Product	Starting Materials	Reference
Structural Concrete (walls, etc.)	Foamed polystyrene (PS) + portland cement.	8
Dunnage (loose or molded)	Reground foamed PS food trays, refoamed, molded.	8
Drainage Pipe	Foamed PS food trays, iron oxide, nucleator for azo foaming agent. "PVC blister packs, bottles, circuit board holders + virgin PVC.	12
Bed Rails	Recycled lead-acid battery cases, 0.5% foaming agent.	17
Fence Posts or Floors for Farm Buildings.	Polyolefin waste (min 50%), up to 20% PVC, 20% paper +foaming agent.	13
Floor Mats, Wheel Chocks, Pads, Truck Bed Liners, Drainage Pipe Telephone Conduit	Copper contaminated wire & cable scrap.	14
Composite Board	Plastics auto scrap, sawdust, (or chopped glass) 5% MDI-isocyanate binder.	15
Polyester Polyols (raw material for polurethane foams)	PET bottle scrap or polyester fiber from discarded clothing, chemically digested.	16
Garbage Bags	Polyolefin waste from household and industrial sources	18
Greenhouse Film	Clean reclaim film blended with linear low density PE	19

U.S. PLASTICS PRODUCTION BILLIONS OF POUNDS

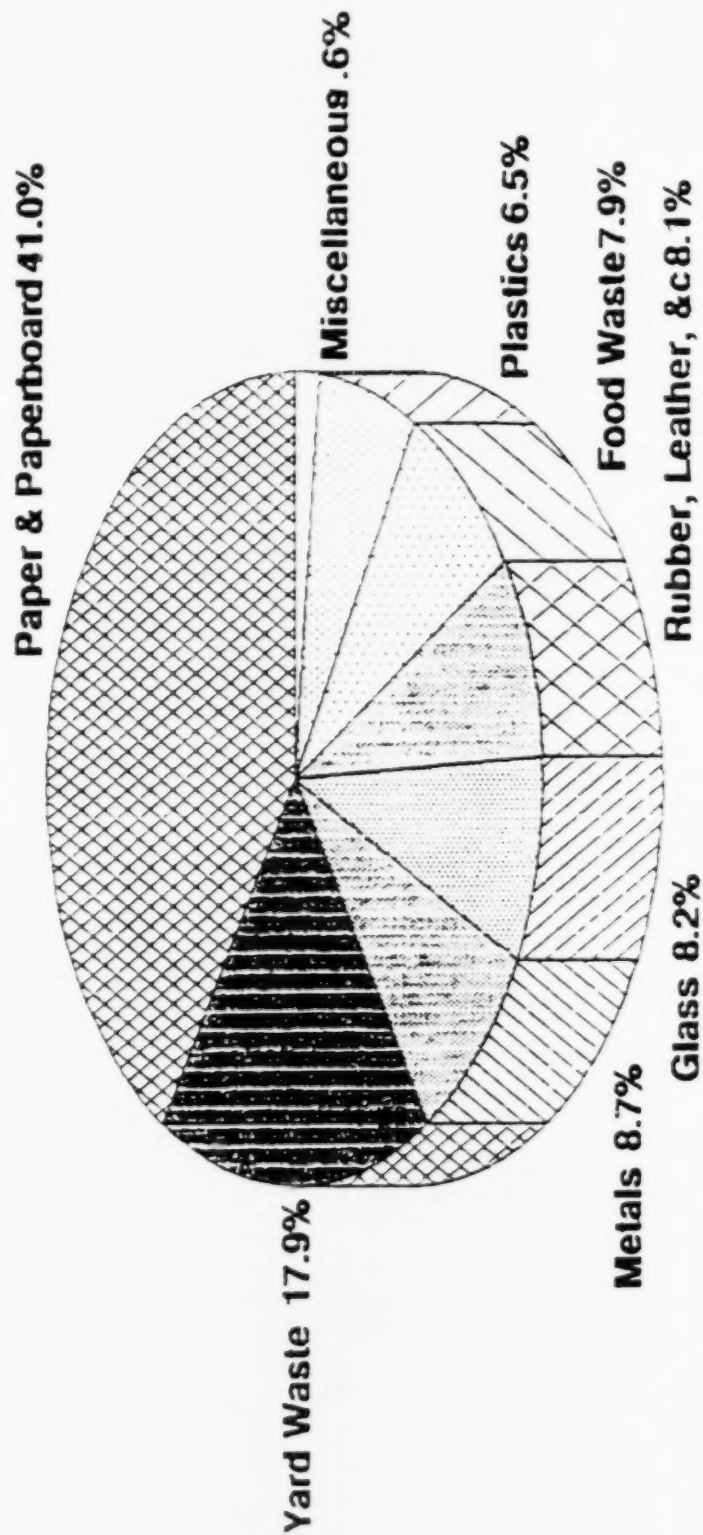


Source: Modern Plastics

FIGURE 1.

COMPOSITION OF MUNICIPAL WASTE

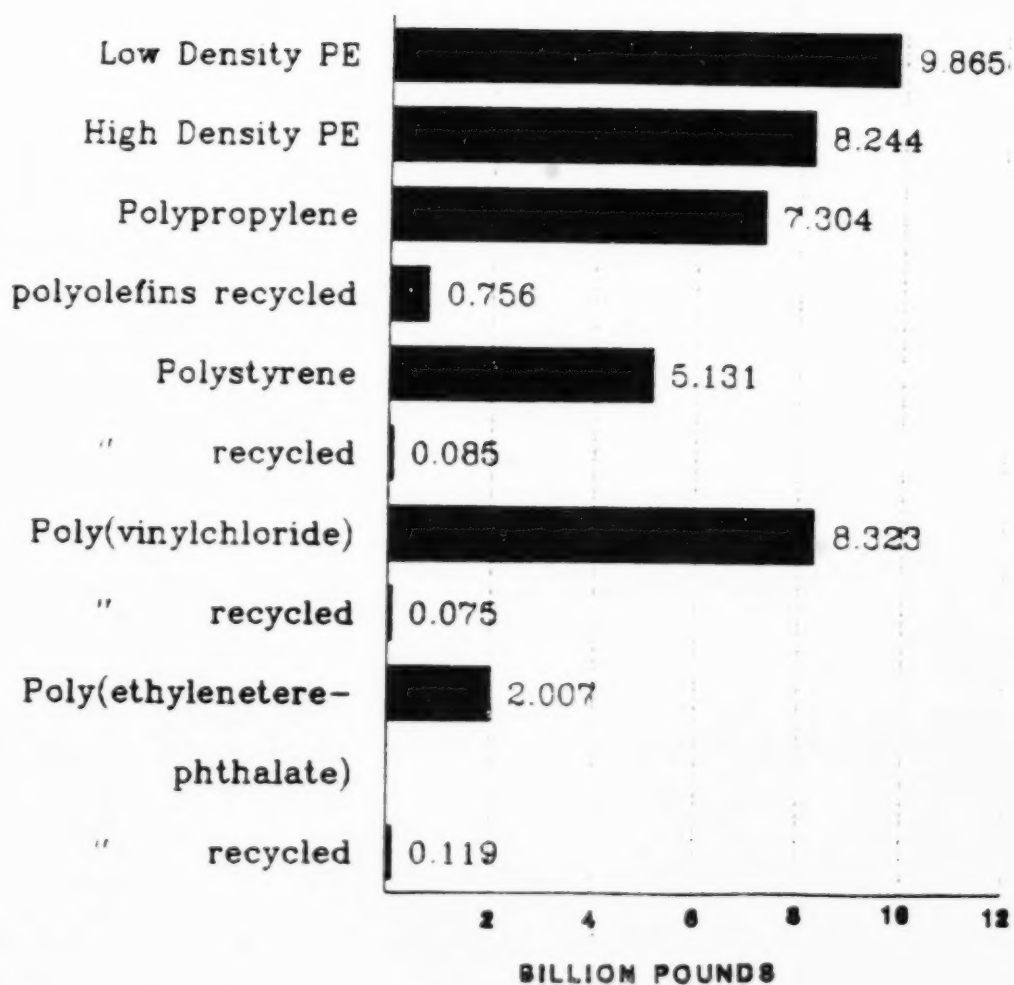
Percent by Weight



Source: U.S. EPA

FIGURE 2

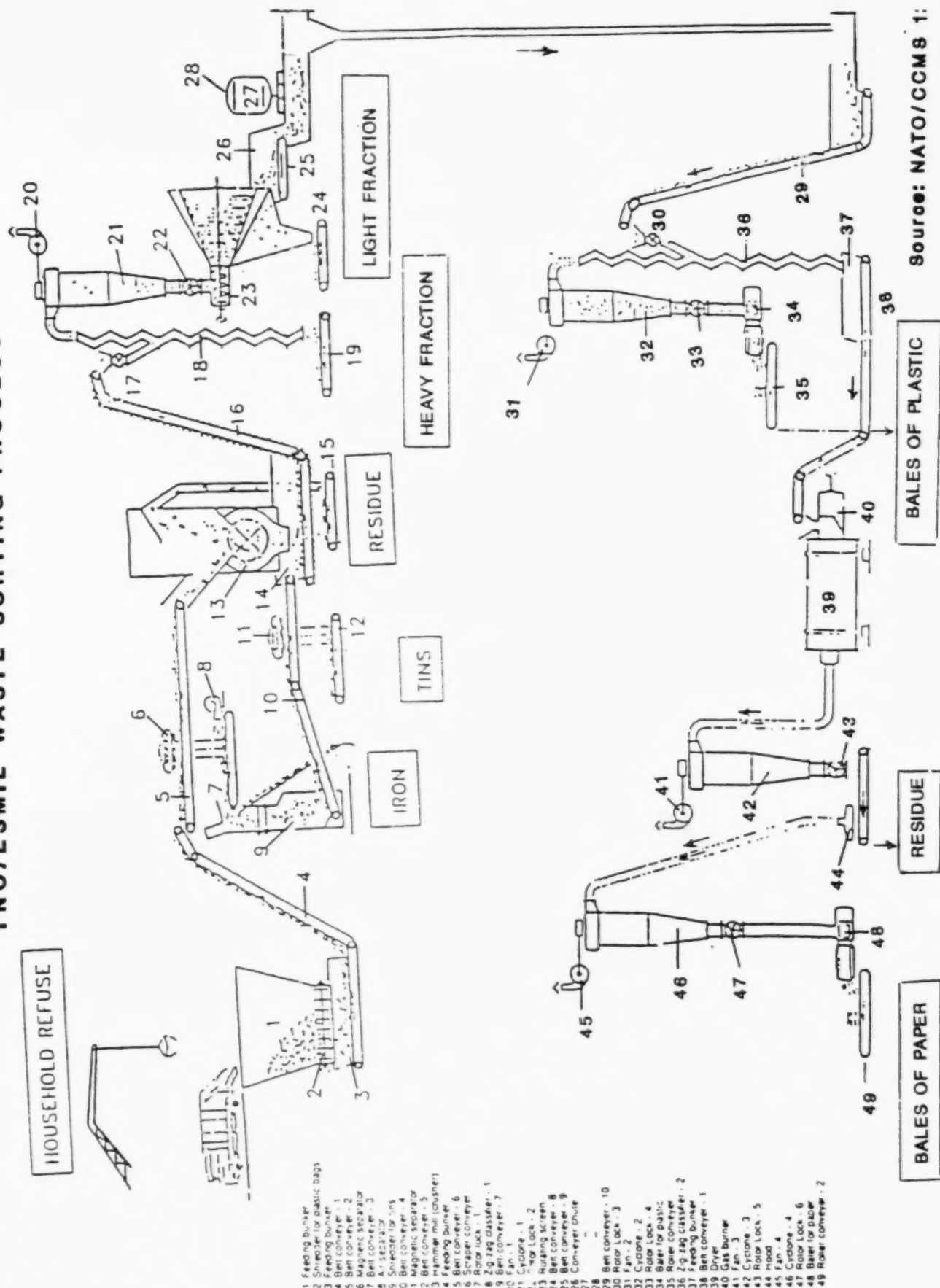
PRODUCTION OF MORE COMMON PLASTICS vs. VOLUME RECYCLED (1988)



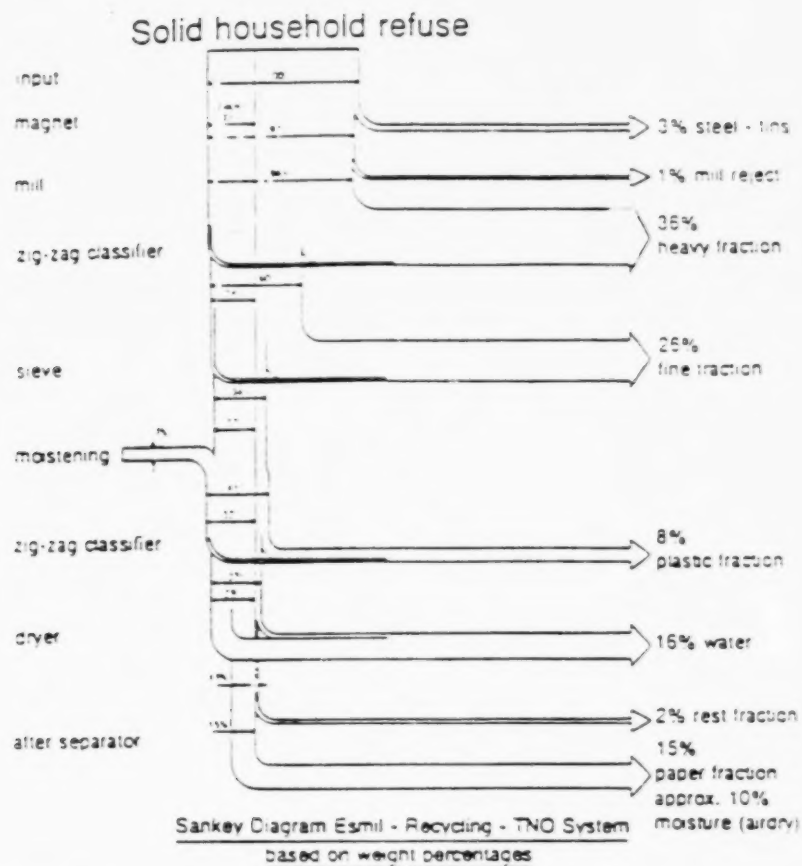
Source: Modern Plastics

FIGURE 3

FIGURE 4
TNO/ESMIL WASTE SORTING PROCESS

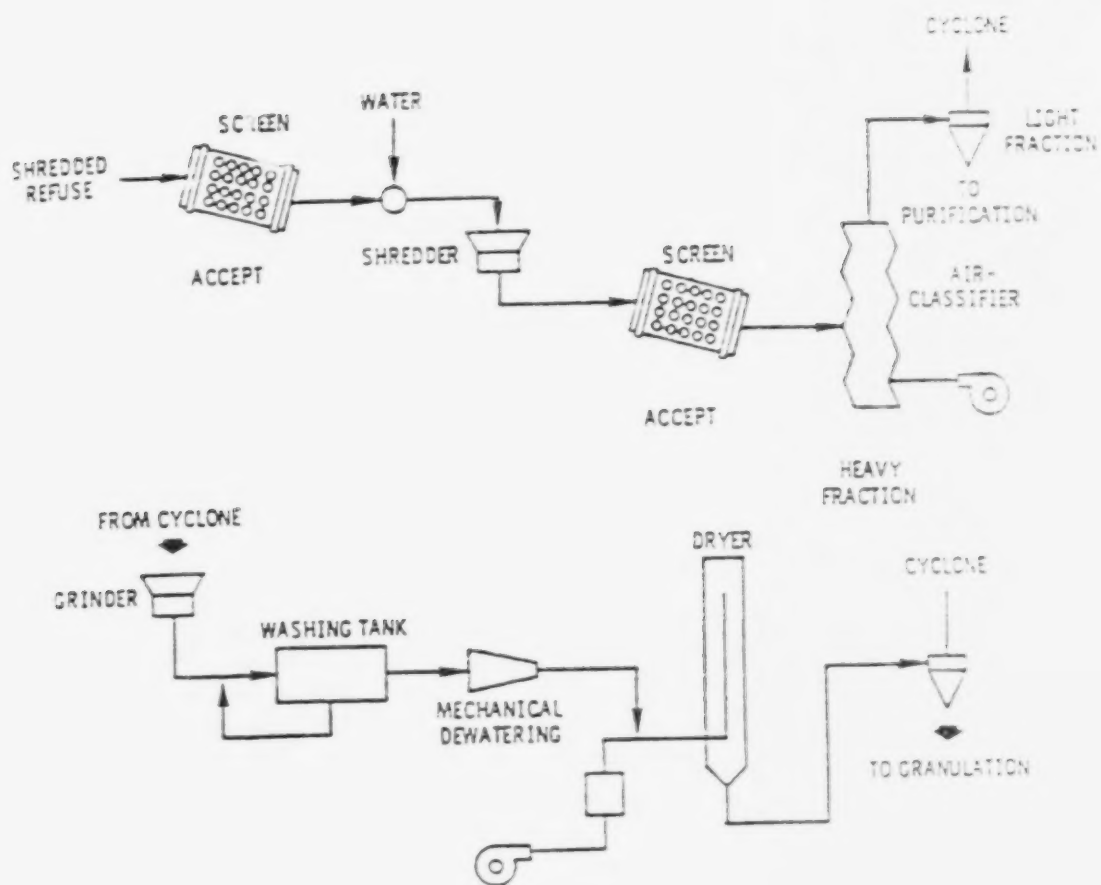


- 1 Feeding Bunker
- 2 Shredder for plastic bags
- 3 Feeding Bunker
- 4 Belt conveyor - 1
- 5 Belt conveyor - 2
- 6 Bag separator
- 7 Bag separator
- 8 Air separator
- 9 Shredder for tins
- 10 Belt conveyor - 4
- 11 Magnetic separator
- 12 Belt conveyor - 5
- 13 Hammer mill (crusher)
- 14 Feeding Bunker
- 15 Belt conveyor - 6
- 16 Rotor lock - 1
- 17 Rotor lock - 2
- 18 2g bag classifier - 1
- 19 2g bag classifier - 2
- 20 Belt conveyor - 7
- 21 Cyclone
- 22 Rotor Lock - 1
- 23 Air Lock - 2
- 24 Hauling Screen
- 25 Belt conveyor - 8
- 26 Belt conveyor - 9
- 27 Conveyor chute
- 28 Belt conveyor - 10
- 29 Rotor Lock - 3
- 30 Rotor Lock - 4
- 31 Fan - 1
- 32 Fan - 2
- 33 Rotor lock
- 34 Roller for plastic
- 35 Roller conveyor
- 36 2g bag classifier - 2
- 37 Feeding Bunker
- 38 Belt conveyor - 1
- 39 Dryer
- 40 Gas burner
- 41 Fan - 3
- 42 Cyclone - 3
- 43 Rotor Lock - 5
- 44 Hood
- 45 Fan - 4
- 46 Rotor lock
- 47 Rotor lock
- 48 Belt for paper
- 49 Roller conveyor - 2



Based on the average composition of the refuse, the plant gives the following results:

	degree of separation on airdry basis	degree of cleanliness
paper	70 - 80%	approx. 5% plastic and straw 0.9% sand
plastic foil	70 - 80%	1% mainly paper
steel-tins	95%	5%
fine fraction	-	-



**PROCESS FOR MECHANICALLY SEPARATING PLASTICS
FROM DOMESTIC WASTE
(SINTEF)**

FIGURE 6



Post-Consumer Waste Collection Systems (Consumer Pre-Sorted)

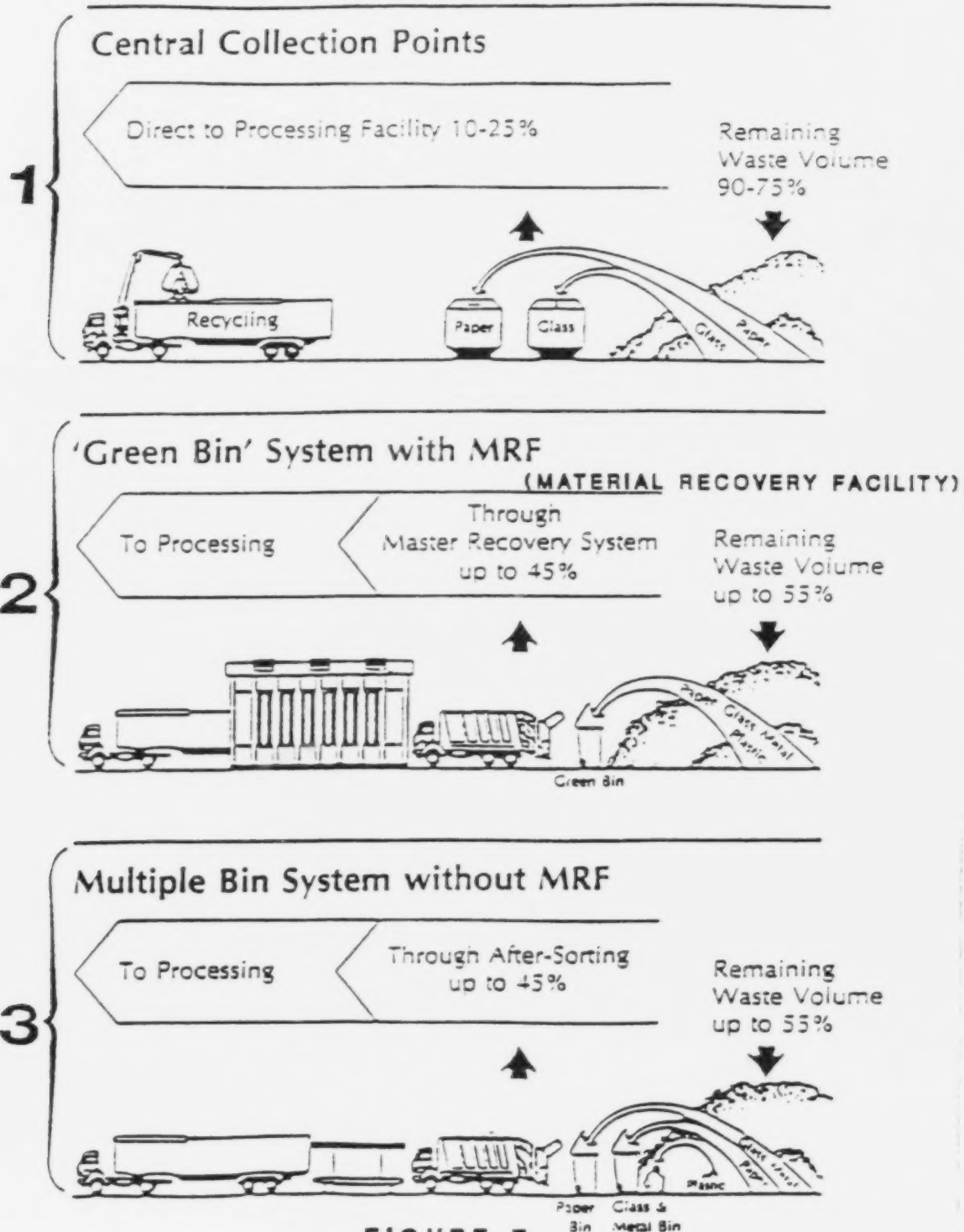


FIGURE 7



AKW Apparate + Verfahren GmbH

Sorting Plant for Green Dustbin and Industrial Waste

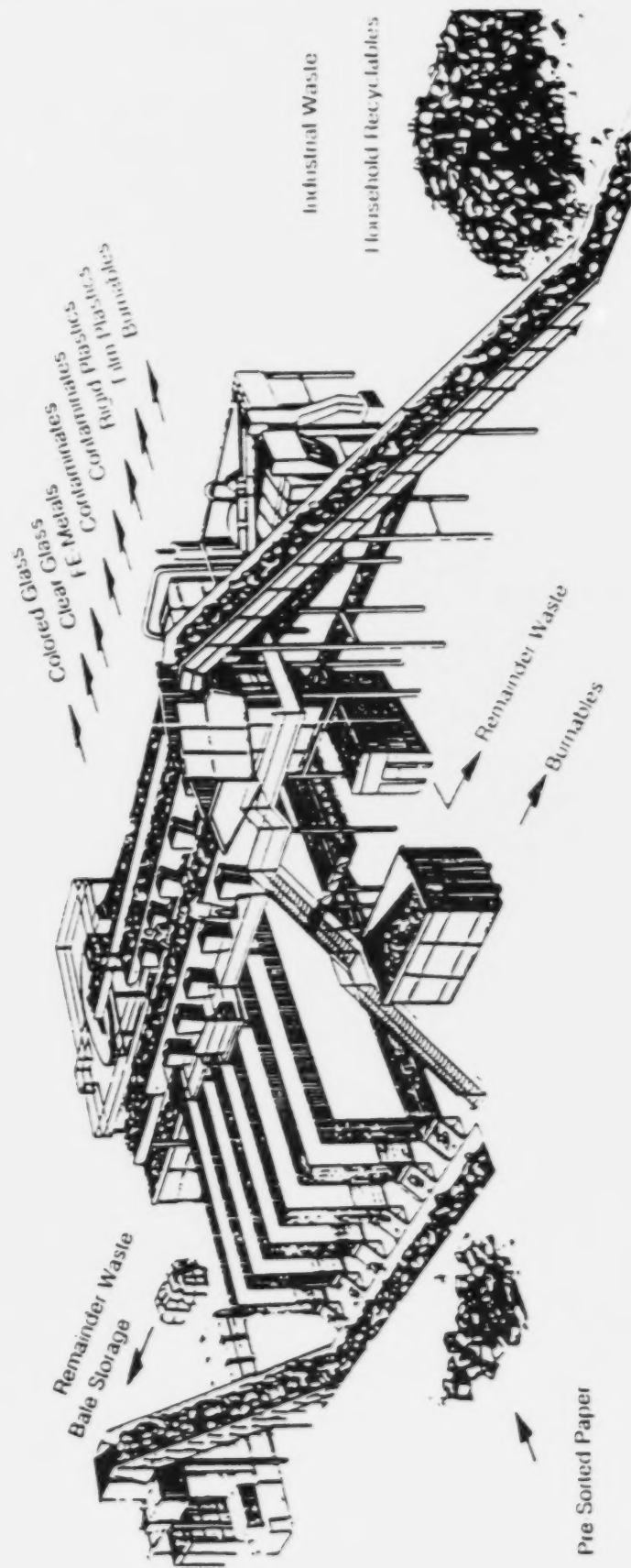


FIGURE 8



HYDROCLONE

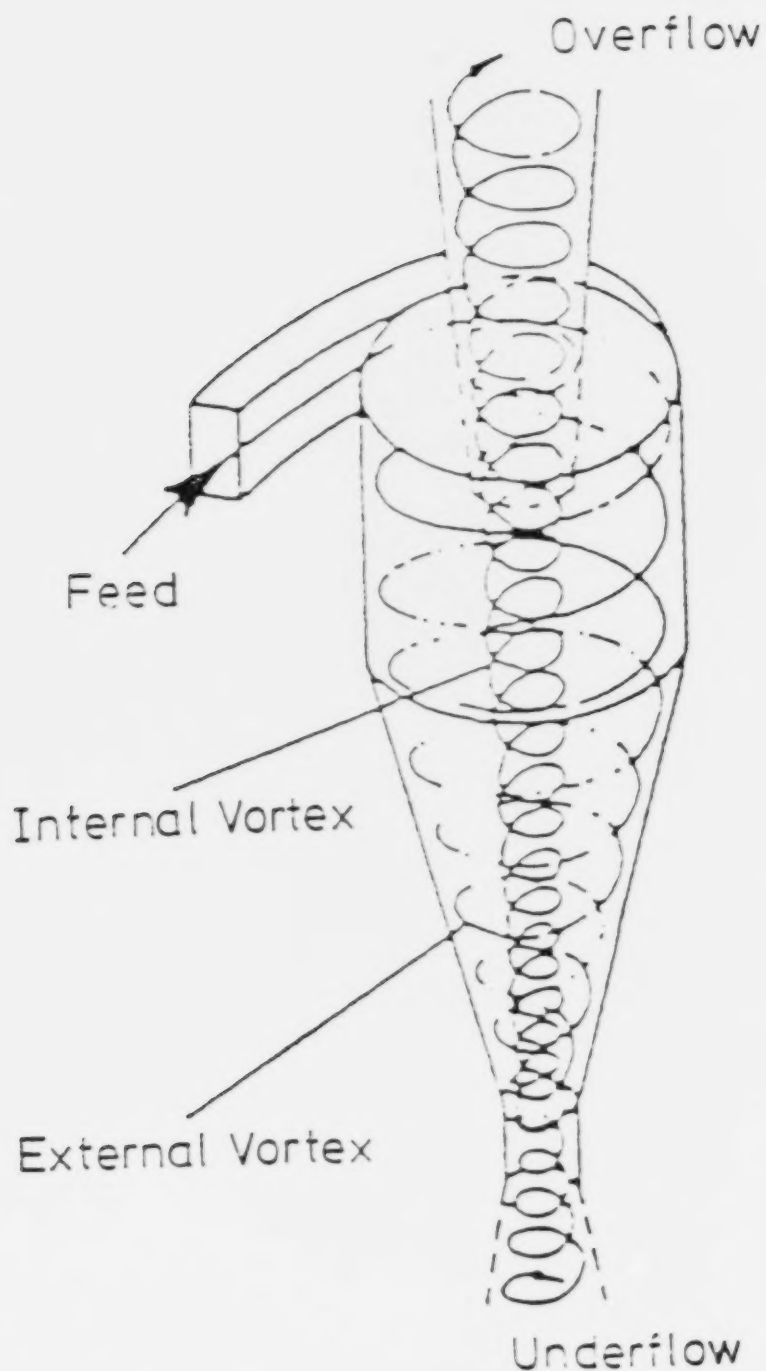


FIGURE 9

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EVALUATION OF EPA WASTE MINIMIZATION ASSESSMENT

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ABSTRACT

EPA's research efforts to encourage the use of waste minimization opportunity assessments is presented in this paper. The early stages of EPA research centered on the development of the EPA-recommended procedure for conducting an assessment, and its use at a number of facilities. This paper will demonstrate the value of the waste minimization assessment for discovering and developing opportunities to minimize wastes by presenting briefs on assessments recently conducted at several private concerns.

These private concerns include a photo lab, a truck manufacturer, a large church facility, a nuclear power generation facility, and a graphic controls manufacturer. These assessments are at various stages of completion. The status and results of each assessment are presented.

Based on completed assessments and discussions with company representatives, the EPA-recommended procedure as described in the "EPA Waste Minimization Opportunity Assessment Manual" is evaluated for its usefulness. Reluctance in initiating an assessment has been encountered, but when technical support was provided to conduct an assessment, company representatives expressed strong satisfaction with the results.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

While the word "assessment" often raises the fear that what is being talked about is an environmental audit, the assessment team is not looking for incidences of facility non-compliance. Their purpose is to examine a process and its components for inspiration to develop techniques that would enhance the cleanliness of a particular process or operation. To accomplish this goal, certain team members must have technical background appropriate to the type of process they are assessing. Therefore, a knowledge of RCRA compliance and SARA Community Right-to-Know regulations is not required of the assessment team.

Conducted by an in-house team or with an independent outside consultant, a waste minimization opportunity assessment (WMOA) is simply a structured review of a process or operation to lead to identified opportunities for waste reduction or recycling. Its focus can be broad or narrow. Often, it is more effective to select a few areas for intensive assessment than to attempt to cover all waste streams and processes at once.

The EPA has published "The Waste Minimization Opportunity Assessment Manual" (EPA/625/7-88/003) for conducting a waste minimization assessment. This manual is available at no cost from the EPA's Pollution Prevention Research Branch, Cincinnati, Ohio 45268. The procedure recommended in the manual is outlined in Figure 1. WMOA's are an extremely effective way to improve a facility's operations, from both an economic and environmental standpoint.

The following sections on industry assessments, "church assessments", and New Jersey assessments represent descriptions of some of the assessment efforts currently being conducted by the EPA.

INDUSTRY ASSESSMENTS

The focus of the industrial assessments effort has been on locating small and medium-sized facilities which may not have the immediate resources or expertise to do what is necessary to reduce their waste and would benefit significantly from Agency support. Toward this goal, assessments have been conducted at a mini-photo lab and a truck manufacturing facility. Both hazardous and non-hazardous wastes are included in the assessments.

Details on the mini-photo lab and the truck manufacturer assessments are provided below.

MINI-PHOTO LAB

After an assessment in August 1989, the assessment team identified five waste minimization options they considered applicable to the waste-streams of interest. Following is a brief description of these options.

Option 1 - Wash Water Control - Wash water is used for color film development and the B&W paper process. The wash water is turned on each production day at approximately 7:00 a.m. and shut off at 7:00 p.m. Water use is therefore continuous during the day, however, production is not. The waste minimization option consists of a simple timer control system consisting of a switch, timer and solenoid valve. The operator would punch a button on the switch to activate the timer. In turn, the activated solenoid would allow water to flow for a preset time period.

Option 2 - Silver Recovery/Metal Replacement Cartridges - Silver is found (as light-sensitive silver halide) in spent photographic chemicals and wash waters as a result of removing the emulsion on films and papers. A metal replacement cartridge is a widely-used device for silver recovery. It can be used alone or in conjunction with other recovery technologies. In this case, the spent process solutions which contain significant amounts of silver would be plumbed to a single pipe. Two cartridges would be used to allow for high capacity while maintaining a high recovery rate.

Option 3 - Silver Recovery/Electrowinning - An electrowinning unit passes a direct current through a concentrated silver solution from anode to cathode causing the silver to plate out onto the cathode in nearly pure metallic form. A wide range of equipment is commercially available for electrowinning. Using manufacturer's literature as a basis, it is expected that up to two batches (4 gallons each) can be treated each day. During the average batch, 1.13 troy oz. of silver would be recovered within 4.5 hours.

Option 4 - Silver Recovery - This option is based on using the electrowinning device in Option 3, with metal replacement cartridges used to polish the effluent. The average effluent will be desilvered from 500 mg/L to approximately 10 mg/L, using only one cartridge.

Option 5 - Bleach Fix Recovery - The recommended method for bleach fix recovery is desilvering with two metal replacement cartridges. This requires three steps: 1) silver recovery, 2) restoring bleaching ability by aerating ferrous-EDTA complex to oxidize back to ferric-EDTA, and 3) replenishment of chemicals lost through carry-over with the film or paper. Approximately 75% of the recovered bleach fix solution can be reused while 25% should be discarded to prevent contaminant build-up.

Total capital investment, net operating cost, and payback period for each option are shown in Table 1. The owner of the lab has received a copy of the final assessment report and is taking the recommended options under advisement.

TABLE 1. SUMMARY OF MINI-PHOTO LAB WASTE MINIMIZATION OPTIONS

WASTE MINIMIZATION OPTION	TOTAL CAP. INVESTMENT, \$	NET OP. COST SAVINGS, \$/YR	PAYBACK PERIOD, YR
Wash Water Control	\$ 675	\$ 1,436	0.47
Silver Recovery Using Metal Replacement Cartridges	1,071	1,325	0.81
Silver Recovery Using Electrowinning	3,510	1,414	2.48
Silver Recovery Using Electrowinning with MRC Tailing	3,667	1,757	2.08
Recycle of Bleach Fix and Silver Using MRCs	1,571	2,508	0.63

TRUCK MANUFACTURER

This truck manufacturing facility produces 34 trucks (tractor-trailer) per day. The production processes are primarily assembly and painting. The current quantities of generated wastes and the associated disposal costs for the first three quarters of 1989 are given below:

	Amount (lb)	Cost of Disposal
Waste Paint	184,860	\$12,957
Pretreatment Sludge	71,020	\$ 9,134
Undercoating	3,375	\$ 2,560
Degreasing Solvent (Chlorinated)	13,060	\$ 5,431
Used Oil	28,275	\$ 105
Paint Sludge	474,960	\$15,132
Housekeeping	3,800	\$ 1,428

The above figures represent a sharp decrease from recent years. The facility has instituted a number of waste minimization measures and cost reduction methods related to good waste management practices.

A site visit was conducted in January 1990 to begin the assessment. Although this facility has made major strides in waste minimization, the assessment team feels there are additional opportunities which may have significant impact. The following are targeted areas which will be investigated further throughout the assessment and feasibility phases.

Spray Painting - Air-assisted airless spray equipment is used for most spray painting. This method is a distinct improvement over conventional compressed air spray painting, however, alternatives exist which may improve transfer efficiency. Increasing the transfer efficiency reduces the volume of paint used and reduces volatile organic carbon (VOC) emissions.

Phosphating - An automated phosphating (conversion coating) process and electro-coat (E-coat) is used for small and medium-sized parts. This line consists of several processing and rinsing steps. The rinse water is piped to a chemical treatment plant where it is combined with paint booth wastewater. The resultant sludge is disposed as a hazardous waste.

It may be possible to avoid waste treatment of the phosphating rinse water by using an ion exchange recycle system, thereby also reducing water usage. Furthermore, the current wastewater treatment process, which uses large amounts of ferric chloride, may be altered, resulting in reduced sludge generation.

Degreasing of Rail Frames - The rail frame, or chassis, is degreased prior to spray painting using a chlorinated solvent (90% 1,1,1-trichloroethane/10% methylene chloride). The spent solvent is distilled (350-400 gallons per day) and reused. Waste minimization options may include chemical substitution, procedural changes, or improvements to the recycle process.

The assessment team is completing the feasibility phase and a draft report is expected in May 1990.

CHURCH ASSESSMENT

This study of a church facility looked at daily office operations, special functions, general maintenance and an on-site pre-school. As would be expected, churches are not normally large waste sources, however, they are a tremendous source of social awareness. It is anticipated that this assessment and suggestions for waste minimization will result in wide-spread distribution through the church's governing bodies and congregation. This information will impact not only other churches, but also people's activities at home and at work.

The location of the church assessment was the Mt. Washington Presbyterian Church (MWPC) which is about fifteen miles east of downtown Cincinnati. With a 1990 budget of \$615,000 and a \$3,000,000 renovation and expansion project, this 2,000-member church represents a substantial institutional facility. The church has a very aggressive Recycling Committee which has been active in collecting recyclable material for the community.

The site visit was made in December 1989. The specific areas of concern included building and grounds maintenance, pre-school, social activities, kitchens, administrative offices, and new building expansion.

Predictably, the largest waste generated by the church is white paper. However, there are numerous other cleaners, paints, lawn materials (e.g., weed killer), etc., that are used in significant quantities. The final report describing waste minimization options is expected to be available by the summer of 1990.

NEW JERSEY ASSESSMENTS

A pilot project with the New Jersey Department of Environmental Protection (NJDEP), entitled "Assessment of Reduction and Recycling Opportunities for Hazardous Waste (ARROW)," will allow the State to evaluate waste minimization techniques and conduct assessments at approximately thirty facilities within New Jersey. The objective of the site selection is to cover ten industries (three sites in each) to develop industry-specific information through the assessment activities.

Through a subcontract with NJDEP, the New Jersey Institute of Technology (NJIT) is locating sites and performing the assessments by following the EPA-recommended procedure outlined in the EPA manual. Participation in the program by facilities is on a voluntary basis. To date, response to the program has been enthusiastic, and 14 companies are lined up for assessment work. Four site visits have been completed and the assessment reports are being prepared. Brief descriptions of two of the companies visited and potential waste minimization options follow below.

NUCLEAR POWER GENERATION FACILITY

Interestingly, the bulk of the wastes from this electrical power generation facility is from construction and maintenance activities when power generation is shut down. Three major sources of waste streams were identified by the assessment team: operations, maintenance, and site services. After analysis of costs and waste generation quantities, the assessment team targeted opportunities for reduction in the levels of off-spec materials and containers of partially used materials which go to waste treatment and disposal. Several waste reduction options were identified, such as improved project estimation and planning of material procurement, dispensing, and stocking; incentives to contractors for waste reduction; and improved security to protect against wastes imported to the site.

GRAPHIC CONTROLS MANUFACTURER

This facility manufactures pens and markers for automatic recording devices and inks for use in these devices. The waste generation data indicate that the operation for ink formulation and preparation contribute to the bulk of the hazardous waste generation. Some options leading to reduced waste generation include reduction in quantities of rinse water used in the cleaning of equipment; improved scheduling of colors and types of batches of inks to reduce cleaning between batches; increased use of mechanical cleaning of tanks to supplement water cleaning; and changes in ink preparation procedure such as the utilization of a large ink base which

could be tinted to the appropriate color in smaller batches as the need arose using small amounts of tinting color.

NJIT continues to work with facilities who show a strong interest in waste minimization and have volunteered to participate in the ARROW program. This effort will continue through August 1991.

ASSESSMENT PROCEDURE EVALUATION

The EPA's assessment procedure itself is of interest regarding its usefulness in identifying waste minimization opportunities. As expected, this issue is difficult to quantify, however, some general comments on the effectiveness of the manual can be made from the assessments that have been completed within the EPA's waste minimization opportunity assessment program.

Discussions between EPA contractors performing waste minimization opportunity assessments and company representatives led to identifying three issues on how a company may be delayed in initiating an assessment effort. These three issues are as follows:

- 1) Implementation of the Manual's procedure is based on the establishment of firm corporate commitment. This commitment is needed in order to devote necessary time and resources. Management may not be approachable if specific information is not available to them on what the company can expect in return for their investment.
- 2) To someone who is not familiar with the manual, it appears cumbersome and lengthy and looks like a lot of work in filling out the forms. This impression may cause users to lay the Manual aside until a later time. The user may or may not return to the Manual.
- 3) Occasionally there is the fear that the completed manual forms would become available to the regulatory agencies and become incriminating information. This unfounded fear prevents people from filling out the forms which is a critical step in understanding a facility's waste generation and management practices.

In situations where outside assistance was received in performing assessments, company representatives expressed strong satisfaction with the results. They perceived the amount of time involved in the exercise to be appropriate. The most valuable result was the identification of ways to lower costs, which in turn helped convince management of the profitability to be incurred in an effective waste minimization program.

It is reasonable to conclude that many manufacturers recognize their waste generation problems and have undertaken actions to address and improve them. Toward this end, they are very receptive to any method such

as the one presented in the Manual which will assist them in meeting their waste management objectives.

CONCLUSION

This paper describes several waste minimization success stories arising from the EPA's Pollution Prevention Research Branch in Cincinnati, Ohio. The programmatic approach has been to go to industry to determine the manual's implementation and to transfer technical pollution prevention impacts throughout the community, especially to small and medium-sized businesses which may not otherwise have the resources to pursue pollution prevention initiatives on their own. Furthermore, it is clear that EPA's program has focused on practical approaches to already existing processes and facilities. Such an approach begs the question: What about the future?

EPA's assessment program will continue to aid in the establishment of a knowledge pool of individuals technically-oriented to pollution prevention. The assessment process is becoming an integral part of business management practices, much as safety concerns have become routine. Beyond these assessments, the Agency's pollution prevention research programs must turn to identifying clean practices, clean products and processes. With the cooperation of representatives from private concerns, EPA anticipates broad potential for research in alternative technologies and products that lower risks to the environment and our future heritage.

WASTE MINIMIZATION ASSESSMENT PROCEDURE

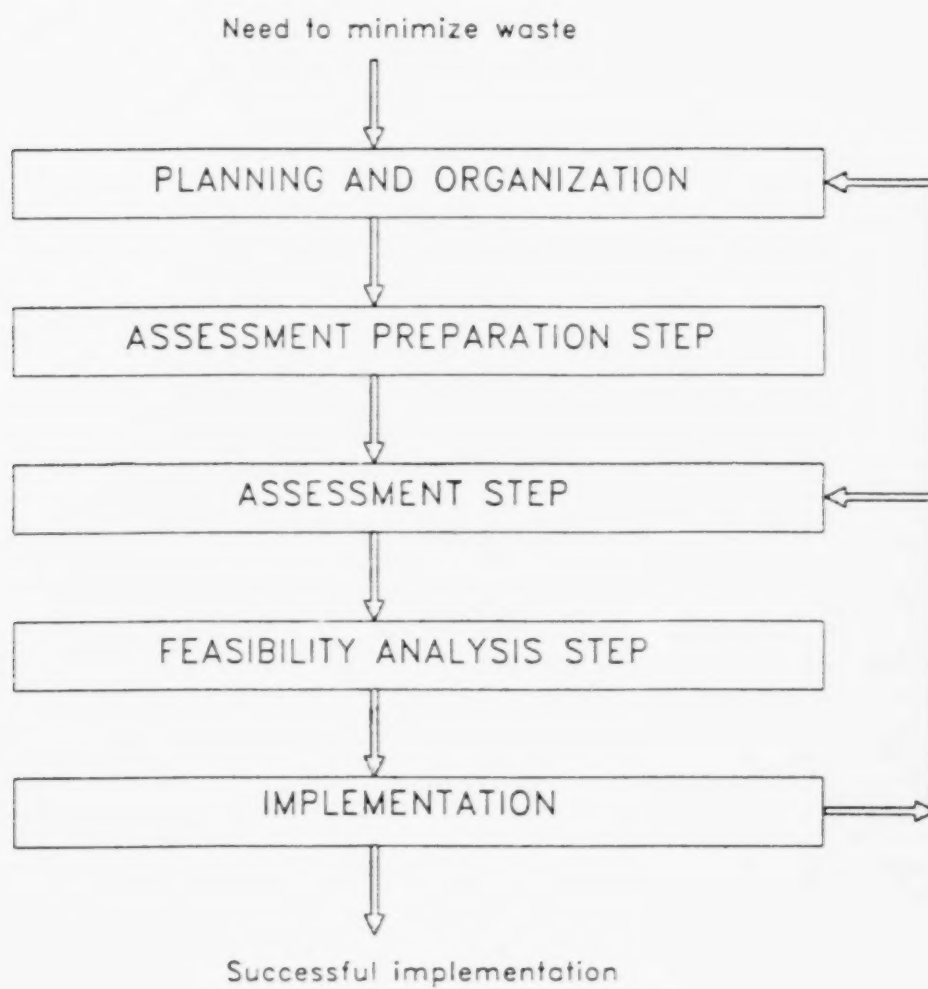


FIGURE 1

SLURRY-BASED BIOTREATMENT OF
STILL BOTTOMS SORBED ONTO SOIL FINES

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ABSTRACT

Research focus is on the biodegradation of organic contaminants on fine fractions, separated from whole soil. Leachates or aqueous extracts from whole soil are of importance, also. Waste activated sludge from conventional secondary treatment provides mixed microbial populations for semi-continuous slurry reactor configurations. To date, operations have been carried out under aerobic conditions. However, at some point, a sequence of aerobic/anaerobic steps will be evaluated. Whole soil samples were obtained from a site immediately adjacent to an impoundment used for disposal of still bottoms. This waste is the residue of benzene, toluene and xylenes (BTX) production by distillation of a high molecular weight petroleum feed stock under strong acid conditions. Chlorinated aromatic wastes have been detected in the otherwise predominantly hydrocarbon material.

Contaminants are a diversity of simple aromatic and extremely complex multi-ring compounds. Thus, relative concentrations of representative compounds are monitored during biodegradation. In many instances, the analytical method of choice is gas or liquid chromatogram peak height, as a function of carrier, instrument temperature program and reference residence time. Feed rate and the addition of phenol as co-substrate are manipulated experimental variables. Significant reductions of marker species concentrations, often to levels below detection limits, are observed with low, medium and some high molecular weight PAH-type compounds, as well as the chlorinated species.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

Distillate bottoms and sludges from a benzene, toluene and xylene (BTX) production process were impounded in two lagoons, over several decades. The process consisted of cracking naphtha in the presence of sulfuric acid. Possible contaminants include, but are not limited to, simple aromatic species, polyaryls species, polynuclear aromatic hydrocarbons (PAHs), as well as sulfonated derivatives of these compounds. One impoundment exceeds ten acres in extent and contains an estimated 100,000 cubic yards of residues. The contents of the lagoon have separated into several distinct layers that include, in bottom-to-top sequence, a solid organic layer, a layer of viscous organic matter, an oil-like layer, and a floating aqueous layer. Many of the waste species have slight solubilities in water and/or affinities for some of the constituents of soil; these have migrated into and through the soil immediately adjacent to and underneath the lagoon. It is the contaminated soil from such adjacent areas that is the subject of this investigation.

The EPA has determined that concentrations of distillate bottoms contaminants must be significantly reduced before the site can be closed. Many methods of soil treatment are possible; these include chemical extraction, incineration, and biological treatment. A number of workers have demonstrated that compounds typically found in distillate bottoms (aromatics, polyaryls, and PAHs) are biodegradable under aerobic conditions. Mass transfer of these compounds from the soil to the microorganisms is usually the most significant barrier to biodegradation processes.

A biotreatment process using slurried soil fines has been developed. The slurry-based system aids mass transfer by facilitating greater contact between contaminated soil and microorganisms. Obtaining the slurry of fines involves a pretreatment process in which whole soil is fractionated; the highly contaminated fractions are prepared as a suspension of soil fines for subsequent biodegradation experiments [1]. Separating the soil fines reduces the mass of material requiring additional treatment. The biological treatment process utilizes a mixed microbial culture in a slurry-based system operated in a semi-continuous manner, under aerobic conditions.

LITERATURE REVIEW

The distillate bottoms contaminants are a complex mixture of polycyclic aromatic hydrocarbons, including aromatic compounds, such as benzene, toluene, and xylene (BTX), and a complex mixture of bi- and polyaryl species, such as bis(p-tolyl)ethane and 1,2-dimethyl-4-phenylmethylbenzene. Bjorseth (1983) describes PAHs as fused five and six member ring compounds in which the interlocked rings have at least two carbon atoms in common [2]. Bi- and polyaryl compounds consist of two or more aromatic rings connected by a single bond from a carbon atom of aromatic ring to a carbon atom of another or to a carbon chain that connects to another aromatic ring.

BTX and sixteen PAHs are considered priority pollutants by the EPA. Mammalian enzymes are thought to metabolize many of these compounds in

carcinogenic substances (Cerniglia, 1984)[3]. For this reason, their presence in soil and potential mobility into groundwater is a matter of great concern. A more detailed discussion of the properties and hazards of PAHs is given by Enzminger and Ahlert [4].

Mackay and Shiu (1977) measured the aqueous solubilities of a number of PAHs at 25C [5]. Table 1 lists the solubilities of some of these compounds. As would be expected, solubility decreases significantly with increasing molecular weight. The aqueous phase concentrations of these and other organic compounds in a system composed of contaminated soil and water is strongly dependent upon adsorptive/desorptive partitioning characteristics with respect to soil constituents, water and biomass. Dzombak and Luthy (1984) discussed the relation between soil organic carbon content and sorption [6]. They cited Lambert's (1965) studies demonstrating that adsorption of neutral pesticides correlated with the organic content of soil [7]. The more organic matter present, the greater the adsorption capacity of soil for organic and nonpolar compounds. Water molecules compete poorly with nonpolar molecules for hydrophobic surface sites in soil organic matter [6].

Table 1: SOLUBILITIES OF TYPICAL PAHs IN WATER [5]

<u>Compound</u>	<u>Number of Rings</u>	<u>Molecular Weight</u>	<u>Molecular Formula</u>	<u>Solubility (ug/L)</u>
Naphthalene	2	128	C ₁₀ H ₈	31700
Acenaphthene	3	154	C ₁₂ H ₁₀	3930
Fluorene	3	166	C ₁₃ H ₁₀	1980
Phenanthrene	3	178	C ₁₄ H ₁₀	1290
Anthracene	3	178	C ₁₄ H ₁₀	73
Fluoranthene	4	202	C ₁₆ H ₁₀	260
Pyrene	4	202	C ₁₆ H ₁₀	135
Chrysene	4	228	C ₁₈ H ₁₂	2.0
Benzo(a)pyrene	5	252	C ₂₀ H ₁₂	3.8
Dibenz(a,h)anthracene	5	278	C ₂₂ H ₁₂	2.5

The solubility and rate of desorption influence bioavailability and have significant effects on the rate and extent of biodegradation. Biological studies have been conducted on a number of PAHs and aromatic species demonstrating the abilities of a variety of microorganisms to metabolize these compounds. Therefore, making the distillate bottoms' contaminants more readily available should have a positive effect on the biodegradation of these compounds.

Bauer and Capone (1985) isolated bacterial populations from intertidal marine sediments capable of aerobic transformations of naphthalene and anthracene [8]. Herbes and Schwall (1977) studied the microbial transformation of these two compounds as well as benzo(a)anthracene and benzo(a)pyrene [9]. They found that two- and three-ring compounds were readily transformed within two weeks while benzo(a)anthracene showed little and benzo(a)pyrene showed virtually no biodegradation after a month. Bauer and Capone (1988) later showed, when a microbial population is preexposed to an individual PAH, the subsequent rate of degradation of that compound is enhanced [10]. They also found that preexposure can enhance the rate of degradation of other PAHs, indicating that selected populations have a broad specificity for PAHs and/or possess common pathways for PAH metabolism. Shocken and Gibson (1984) used *Beijerinckia* sp. grown on biphenyl to co-oxidize acenaphthene and acenaphthylene [11]. Mihelcic and Luthy (1988) compared the microbial degradation of naphthol, naphthalene and acenaphthene under aerobic, anaerobic and denitrifying conditions [12]. All three compounds were degraded quickly under aerobic conditions and more slowly under denitrifying conditions; only naphthol was degraded under anaerobic conditions.

Within the last two years, evidence for biodegradation of higher molecular weight compounds has been reported. Shiaris (1989) measured rates of transformation of benzo(a)pyrene in Boston Harbor [MA] sediments, and observed half-lives of 53.7 and 82.3 days [13]. Heitkamp, et al. (1988) observed the degradation of pyrene into dihydrodiols and pyrenols by *Mycobacterium* sp. [14]. Heitkamp and Cerniglia (1989) later showed that in addition to transforming pyrene, *Mycobacteria* play a significant role in the mineralization of benzo(a)pyrene [15].

MATERIALS AND METHODS

The soil slurry used for present experiments was prepared by the method described by Ahlert, Kosson and Black (1989) [1]. The final separation step was changed from filtration through a ten-micron mesh to gravity settling followed by siphoning the slurry from the top of the settling vessel. This modification enabled larger quantities of slurry to be prepared at one time. The initial extraction, carried out in a rapidly stirred five-gallon plastic-lined pail, did not at first generate the third tar-like organic phase observed in smaller scale experiments. This was corrected by returning to screening. Gravity settling led to great variability in contaminant levels and soil particle size distributions.

This screening method isolates from 5000 to 18000 milligrams of organic material per kilogram of whole dry soil. Assuming the tarry materials is 92% carbon and recovery is approximately 50%, the TOC of the whole dried soil is of the order of 20000 mg/kg or about 2%. The Total Volatile Solids (TVS) of whole dried soil is 49000 mg/kg or 4.9%. Considering the apparent strength of binding and the difficulty of separation, this agreement seems excellent. Five percent is probably an approximate upper bound on the contaminant level of whole soil.

Bioreactors have a working volume of two liters and are filled initially with 50% (one liter) soil slurry, 33% (two-thirds liter) of aerobic culture and 17% (one-third liter) of mineral salts medium. The slurry contains between 30 and 40 g/L of soil fines. If soil fines represent about 40% of the contaminants on whole soil, this corresponds to 60 to 80 mg of contaminants per liter. The composition of the mineral salts medium is that required to achieve the following concentrations of salts in the final reactor mix: ammonium sulfate, 500 mg/L; magnesium sulfate, 100 mg/L; ferric chloride, 0.5 mg/L; manganese sulfate, 10 mg/L; potassium phosphate (dibasic) (cometabolism experiments) 100 mg/L. Humidified air is sparged into the bottom of the reactors. Effluent gas passes through a condenser and condensate is returned periodically to the reactor. Reactor pH is maintained between 6.5 and 7.0 by automatic addition of 0.15 M sodium hydroxide by means of a pH controller.

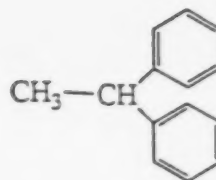
The reactor feeding procedure involves withdrawing 600 mL of well-mixed reactor contents and replacement with 600 mL of slurry stock, seed and mineral medium. Feed corresponds to the initial composition in the reactor, consisting of 50% (300 mL) soil slurry, 33% (200 mL) of water and 17% (100 mL) of mineral salts medium. The initial feeding frequency was daily; this was subsequently changed to every other and, eventually, every third day. This protocol was used for semi-continuous experiments with no cosubstrate. The feeding frequency for experiments in which phenol was used as a cosubstrate with the soil contaminants, was every third day.

Concentrations of the soil contaminants were determined by extracting samples of the reactor contents (25 mL) with cyclohexane (5 mL), followed by High Performance Liquid Chromatograph (HPLC) analysis. Samples were extracted once; replicate assays were carried out on each extract. An extraction of the stock soil slurry indicated removal of some contaminants to levels below the HPLC detection limit, i.e., reductions of 75 to 90%. Serial extractions of the soil slurry demonstrated that the first extraction removed at least 90% of the extractable contaminants. Parallel extractions must be carried out to determine the accuracy of this separation procedure.

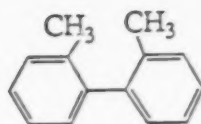
HPLC analysis confirmed the presence of numerous aromatic species and higher molecular weight compounds. Chromatographs display a virtual continuum of peaks with retention times between 8.3 and 22 minutes. Many compounds were identified by matching retention times with a Standard. Subsequent GC/MS analysis identified a number of aromatic and biaryl species. The names and structures of some of the most abundant species are shown in Figure 1. The two largest peaks in the solvent extract were found to be 1,1-bis(p-tolyl)-ethane and 1,2-dimethyl-4-(phenylmethyl) benzene. These identifications were assigned to the two large, corresponding peaks in the HPLC chromatographs. In most cases, reactor performance was referred to HPLC retention times, as distinguished from specific compound identities.



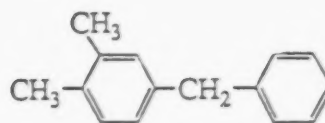
Naphthalene
($C_{10}H_8$, MW=128)



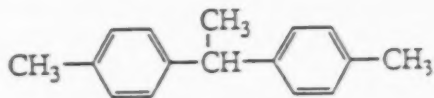
Benzene, 1,1'-ethyldenebis
($C_{14}H_{14}$, MW=182)



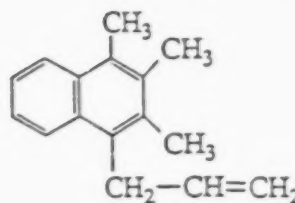
1,1'-Biphenyl, 2,2'-Dimethyl-
($C_{16}H_{14}$, MW=182)



Benzene, 1,2-dimethyl-
4-(phenylmethyl)-
($C_{15}H_{16}$, MW=196)



1,1-Di-(p-toyl)ethane
($C_{18}H_{18}$, MW=210)



Naphthalene, 1,2,3-trimethyl-
4-propenyl
($C_{18}H_{18}$, MW=210)

Figure 1. Names and Structures of Most Abundant
Distillate Bottoms Contaminants

RESULTS

VOLATILITY STUDIES

A study was carried out to determine which, if any, volatile or semi-volatile compounds were being stripped from the slurry. HPLC analysis indicated that benzene is completely removed in four days, while concentrations of toluene remain relatively constant. The large peak corresponding to the xylene isomers and ethyl benzene masked the naphthalene peak at the beginning of the study. After one day, the peak corresponding to xylene/ethyl benzene had essentially disappeared, exposing the naphthalene peak. Naphthalene and other medium molecular weight compounds decreased between 30 and 50% during the four-day study. Non-volatile, high molecular weight compounds exhibited reductions of 10 to 20%, indicating a second phenomena such as indigenous microbial activity was playing a role in contaminant reduction.

SEMI-CONTINUOUS FERMENTATIONS - WITHOUT COSUBSTRATE

Results are reported for Reactor 2. They can be grouped into three categories: a) complete or almost complete degradation [Figures 2 and 3], b) no detectable degradation [often characterized by extremely irregular chromatograph patterns - also, see Figure 4], and c) significant degradation after extended lag [see Figure 5 with lag exceeding 20 days]. Naphthalene, xylene, and ethyl benzene levels were below HPLC detection limits, after a bioreaction interval as short as one day. The magnitude of this reduction indicates that, after accounting for stripping, microbial reactions still play a significant role in the reduction of these compounds, especially naphthalene. Other compounds that were virtually completely degraded, with little if any evidence for stripping, were species with HPLC retention times of 11.94 min, 13.26 min (1,2-Dimethyl-4-phenylmethyl-benzene), 13.86 min, 15.16 min [1,1-Bis-(p-tolyl)-ethane], and 15.87 min. Compounds displaying partial reduction had HPLC retention times of 10.61 and 14.42 min, respectively.

The compound with a retention time of 12.47 min displayed a period of low reaction followed by recovery. This may have been the result of a shift in microbial population distribution; wash-out of one class of organisms followed by rapid growth of another class may have occurred. Compounds having molecular weights of at least 210, i.e., those with retention times of at least 16.00 min, exhibited scattering indicative of a total lack of biodegradative activity. Extending the biodegradation interval, i.e., reducing the feeding frequency, increased the extent of biodegradation of heavier compounds - those with corresponding retention times of 14.47, 15.16 and 15.87 min.

Extracts of reactor contents exhibited significant variability. Inadequate mixing of the stock slurry prior to reactor feed preparation probably resulted in erratic contaminant levels in reactor solutions. It is extremely important that the stock solution be mixed thoroughly in all future

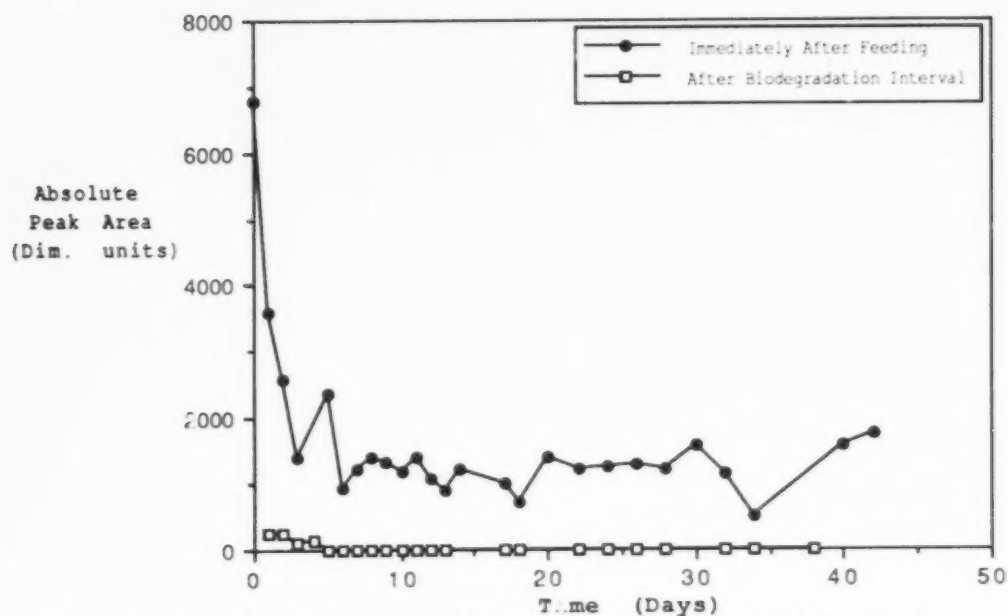


Figure 2: Relative Contamination vs Time for Reactor 2 with No Cosubstrate Added. Results for peak with HPLC Retention Time of 13.26 minutes, tentatively identified as 1,2-dimethyl-4-phenylmethyl-benzene.

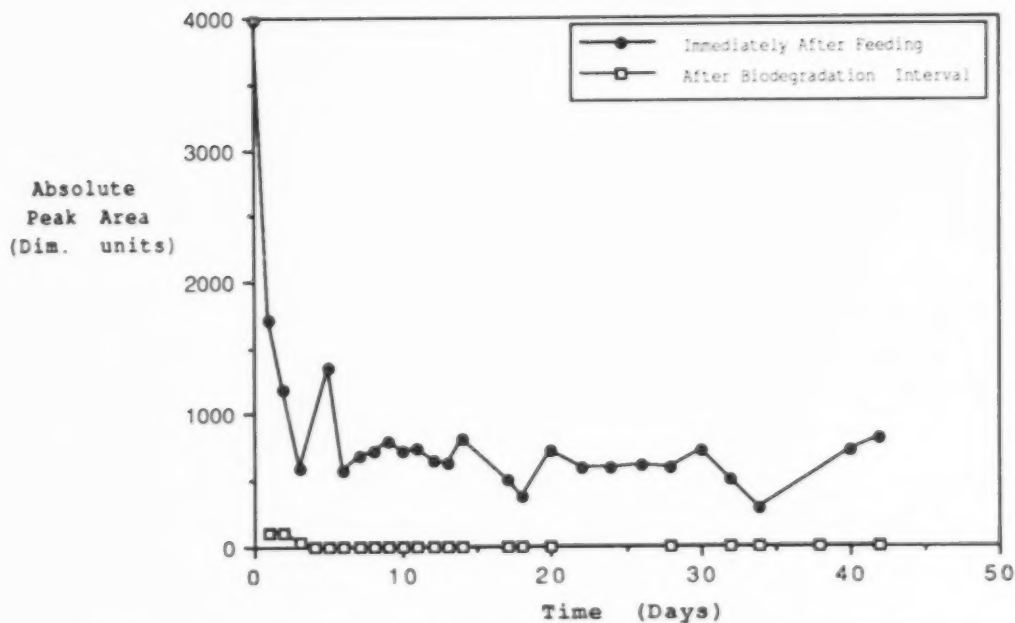


Figure 3: Relative Contamination vs Time for Reactor 2 with No cosubstrate Added. Results for peak with HPLC Retention Time of 13.86 minutes.

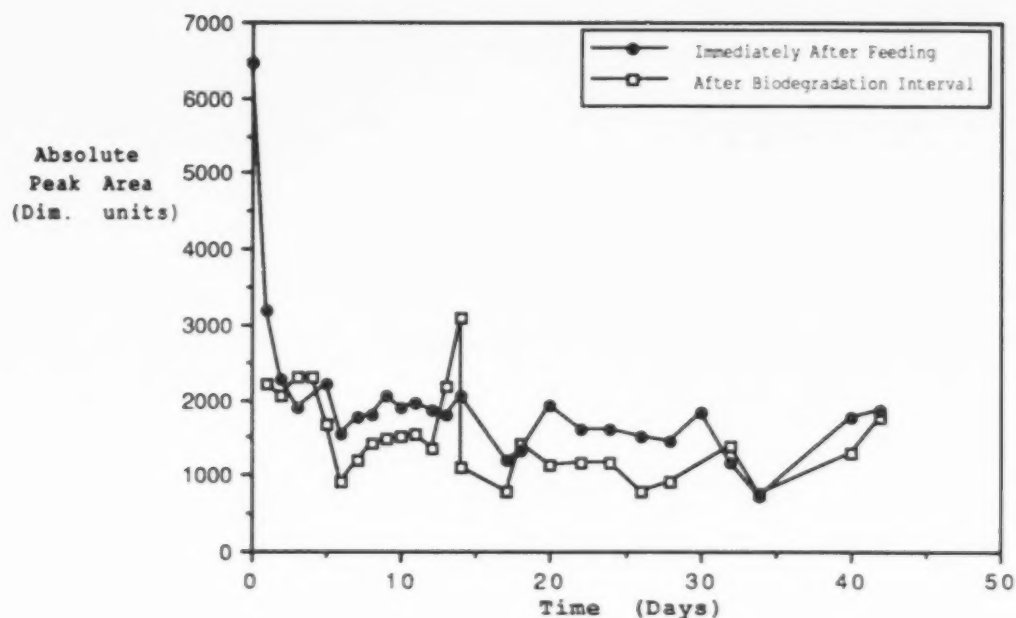


Figure 4: Relative Concentration vs Time for Reactor 2 with No Cosubstrate Added. Results for peak with Retention Time of 14.42 minutes.

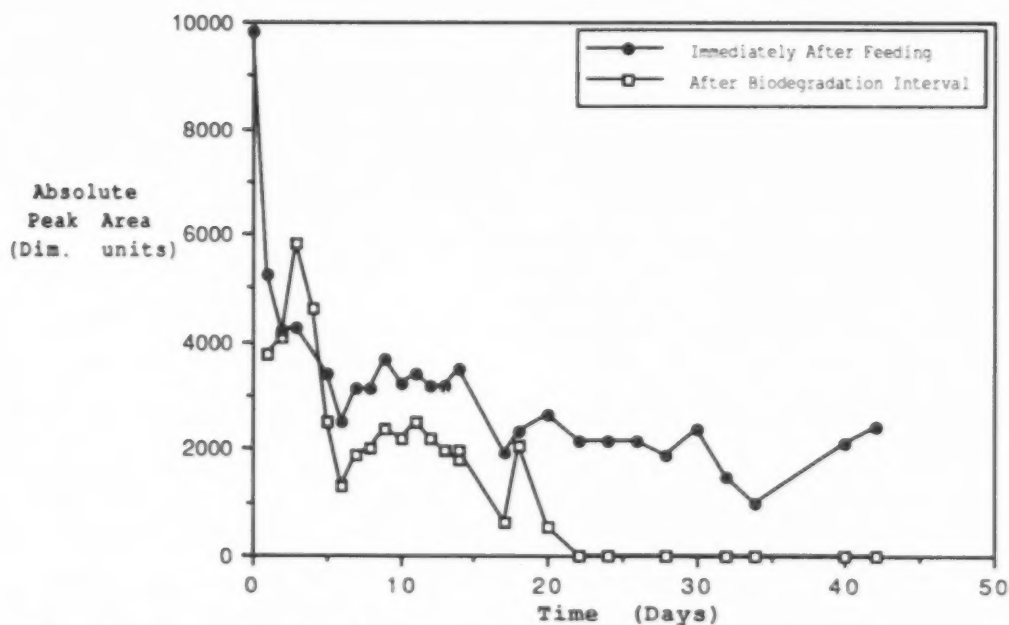


Figure 5: Relative Concentration vs Time for Reactor 2 with No Cosubstrate Added. Results for peak with HPLC Retention Time of 15.16 minutes, tentatively identified as 1,1-Bis(p-tolyl)ethane.

experiments. Variations in reactor volume due to fluctuating aeration and humidification of influent air, affected the relative mass of reactor contents removed prior to feeding. In turn, this caused variations in contaminant concentrations immediately after feeding and after the biodegradation interval. The variations described above resulted in the following deviations from optimal reactor performance: 1) poor reactor agitation caused soil settling and the high soil content in the bottoms of the reactors (where samples are taken) led to unusually high concentrations to be measured after the degradation interval 2) either a low soil content in feed solution caused by poor mixing of the stock slurry solution or water mixed in with cyclohexane extract and subsequent improper HPLC sampling and analysis, resulted in unusually low compound concentration measurements in samples taken immediately after feeding.

SEMI-CONTINUOUS FERMENTATIONS - WITH PHENOL AS COSUBSTRATE

Fermentations with phenol present as cosubstrate were run in duplicate and are referred to as Reactors 2 and 3. The Reactor 2 experiment with phenol was carried out in the same reaction system as the Reactor 2 without substrate. As for the experiment with no cosubstrate, low and medium molecular weight compounds exhibited significant (often total) reductions - retention times of 8.49, 10.61, 11.94, 12.47, 13.26 and 13.87 min.

With phenol added, Reactor 2 displayed substantial degradation of the compound with an HPLC Retention Time of 14.42 min, early in the experiment. Reactor 3 may have had some initial activity, also. In later stages of reactor operation, neither system displayed significant activity. These observations may be attributable to i) a shift in microbial distribution or ii) depletion of phenol and consequent loss of a cometabolic contribution. After an initial lag of 20 to 30 days, 1,1-Bis(p-tolyl)ethane [BTA] appeared to be degraded completely, with or without the addition of phenol. However, an intermediate period of little or no conversion was observed and the length of this period of inactivity was significantly longer (an order-of-magnitude) with phenol present. This effect was probably a consequence of microbial acclimation or population displacement. High molecular weight compounds, with HPLC retention times exceeding 15.87 min, exhibited virtually no reduction.

Increasing feed concentrations at the end of the phenol experiment were attributed to the remaining slurry stock (bottom of the jar) having a much higher soil content than was used for most of the earlier feed solution preparations. It appears that the addition of phenol did not appreciably improve the performance of the bioreactors for degradation of hydrocarbon contaminants of high molecular weight. It did appear to have some influence on the degradation of species of mid-range molecular weight, i.e., BTA.

CONCLUSIONS

Polynuclear aromatic, polyaryl and chlorinated hydrocarbons are associated with the finer fractions of contaminated soil, i.e., natural organic matter and clays. Slurry preparation, with suspension of fines and settling of larger particles, leads to contaminant enrichment of the fines.

A separate tar-like fraction appears during suspension and settling.

Aliquots taken from large volumes (master batches) of soil fines suspensions are highly variable. Samples drawn from slurry bioreactors, for assays of relative contaminant concentrations, dispersed microbial populations and nutrient concentrations, are variable, also.

Microbial degradation rates are strongly correlated with contaminant molecular weight. Over periods of days, slurry reactions yield three distinct results: complete degradation, complete degradation after several days lag, and no detectable reduction in contaminant concentration.

Species with molecular weights exceeding 200, based on HPLC detection limits and retention times, resist microbial reaction.

Phenol appears to have little effect as a cosubstrate.

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ANAEROBIC TREATMENT OF LEACHATE

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ABSTRACT

An upflow anaerobic filter (volume: 800 gal. and empty bed contact time: 3.7 days) followed by a conventional activated sludge system (HRT: 5.6 hr. and SRT: 8 days) was used to determine the fate and effect of hazardous leachate in anaerobic-aerobic systems. The leachate flowrate to the anaerobic filter was 0.15 gpm. Screened raw municipal wastewater (0.85 gpm) and the filter effluent were added to the conventional activated sludge system. Selected organic compounds and heavy metals were spiked to the synthetic leachate (C-source: acetate, propionate, and butyrate, total feed COD: 1600 mg/L) to simulate a typical hazardous leachate.

The results showed that selected heavy metals at design concentrations did not cause any adverse effects on the anaerobic process. Among the organic toxicants the removals of chlorobenzene and toluene were low (15-25%) whereas the removals of acetone, methyl ethyl ketone, methyl isobutyl ketone, trichloroethylene, methylene chloride, and 1,1-dichloroethane exceeded 90 percent. The removal of all added organic compounds by the combined anaerobic-aerobic process exceeded 90 percent. Hence, an upflow anaerobic filter preceding a conventional activated sludge process appears to be effective in treating hazardous leachates.

INTRODUCTION

The objective of this research was to obtain information on the treatability of hazardous leachates in publicly owned treatment works (POTWs). The hypothesis was that a combined anaerobic-aerobic biological treatment process should be able to biodegrade most of the organic compounds present in hazardous leachates. It is well known from literature that some organics such as chlorinated hydrocarbons can be biodegraded efficiently by anaerobic processes. Anaerobic reductive halogenation has been recognized as a possible biotransformation mechanism for chlorinated aliphatic hydrocarbons (1-4).

Aromatic volatile organic compounds, whether homocyclic or heterocyclic, present a special problem to anaerobes because of their ring structure. Evans (5) concluded that the benzene nucleus is first reduced and then cleaved by hydrolysis to yield aliphatic acids which in turn could enter common anaerobic pathways leading to the final products of carbon dioxide and methane. Through the use of ^{18}O -labeled water, it has been shown that oxygen from water is incorporated into anaerobic fermentative transformation of toluene and benzene (6). The same researchers proposed degradation sequences for the transformation of toluene and benzene by mixed methanogenic cultures (7). In contrast, Schink (8) reported no indication of methanogenic degradation for a number of compounds, including toluene and benzene.

A summary of recent work on anaerobic processes for transformation of volatile compounds is presented in Table 1.

TABLE 1. ANAEROBIC TRANSFORMATION OF VOLATILE ORGANIC COMPOUNDS

<u>Compound</u>	<u>Product(s)</u>	<u>Reference</u>
chloroform	carbon dioxide	1
carbon tetrachloride	carbon dioxide	i
	chloroform	8, 9
1,1-dichloroethane	chloroethane	10
1,2-dichloroethane	*	11
1,1,1-trichloroethane	1,1-dichloroethane	9
	*	1, 12, 13
1,1,2,2-tetrachloroethane	1,1,2-trichloroethane	1
chloroethene	carbon dioxide	3
dichloroethene	chloroethene	3, 12, 13
trichloroethene	dichloroethene	3, 9, 13, 14
tetrachloroethene	trichloroethene	13
benzene	carbon dioxide	6, 7, 15
	methane	
toluene	carbon dioxide	6, 7, 15
	methane	

* Products not identified

Recent process and serum bottle studies with semivolatile and/or nonvolatile organic compounds are summarized in Table 2.

TABLE 2. RECENT INVESTIGATIONS OF ANAEROBIC PROCESSES

<u>Investigator(s)</u>	<u>Study</u>	<u>Pollutants</u>	<u>Reference</u>
Blum et al. (1986)	anaerobic filters with coal conversion wastewater constituents	phenolics	(16)
Kuhn et al. (1985)	laboratory aquifer columns to simulate groundwater infiltration	dichlorobenzenes dimethylbenzenes	(17)
Lema et al. (1987)	bench-scale digesters with landfill leachate	unspecified organics	(18)
Suidan et al. (1987)	anaerobic filters with coal gasification wastewater (synthetic)	aromatics	(19)
Boyd et al. (1983)	serum bottle assays to determine fate	phenolics	(20)
Hickey et al. (1987)	serum bottle assays to monitor CH ₄ , H ₂ from pulse addition	chloroform formaldehyde bromoethanesulfonic acid trichloroacetic acid	(21)
Johnson & Young (1983)	serum bottle assay in synthetic sludge for inhibition and recovery	semi-volatile priority pollutants	(22)
Shelton et al. (1984)	serum bottle assay to determine degradability and pathway	phthalates	(23)
Venkataramani et al. (1986)	serum bottle assay of high-strength industrial landfill leachate	not specified	(24)

The fate of both volatile and semivolatile organics in anaerobic digestion of primary and secondary sludge containing sorbed compounds has been described (25).

Several studies have been conducted on the removal and fate of specific organics by conventional primary/activated treatment (26-32). A combined

anaerobic-aerobic process should have the advantages of both processes in terms of capability to biodegrade specific compounds. The goal of this research project was to verify this hypothesis for biological treatment of hazardous leachate.

MATERIALS AND METHODS

Selection of leachate constituents to be used for experimental fate studies was based on survey results of actual hazardous waste sites. The organic compounds and heavy metals which were representative of a "typical" hazardous waste leachate are shown in Table 3 along with the recommended concentrations to be tested.

TABLE 3. LEACHATE CONSTITUENTS

CONSTITUENT	CONCENTRATION, $\mu\text{g/L}$
Acetone	10,000
Methyl ethyl ketone	5,000
Methyl isobutyl ketone	1,000
Chloroform	10,000
Trichloroethylene	400
Methylene chloride	1,200
1,1-Dichloroethane	100
Chlorobenzene	1,100
Toluene	8,000
Ethylbenzene	600
Dibutyl phthalate	200
Bis (2-ethylhexyl) phthalate	100
Nitrobenzene	500
Trichlorobenzene	200
Phenol	2,600
Aluminum	30,000
Copper	100
Iron	500,000
Lead	400
Magnesium	180,000
Manganese	65,000
Nickel	1,500
Zinc	1,000

The leachate constituents were spiked to a synthetic feed to simulate real life hazardous leachate. The synthetic feed prepared in tap water had a design Biological Oxygen Demand (BOD) or Chemical Oxygen Demand (COD) of approximately 2,000 mg/L derived from added acetic and propionic acids.

The anaerobic system consisted of an 800-gallon upflow anaerobic filter packed with plastic media and had a flowrate of about 216 gpd (0.15 gpm). The empty bed contact time was 3.7 days. The effluent of the filter was mixed with about 0.85 gpm of raw wastewater. The total flow of 1 gpm was added to the primary clarifier of the activated sludge system. The solids retention time in the aeration tank was about 8 days and the hydraulic retention time was 5.6 hours. A schematic of the anaerobic-aerobic process is shown in Figure 1.

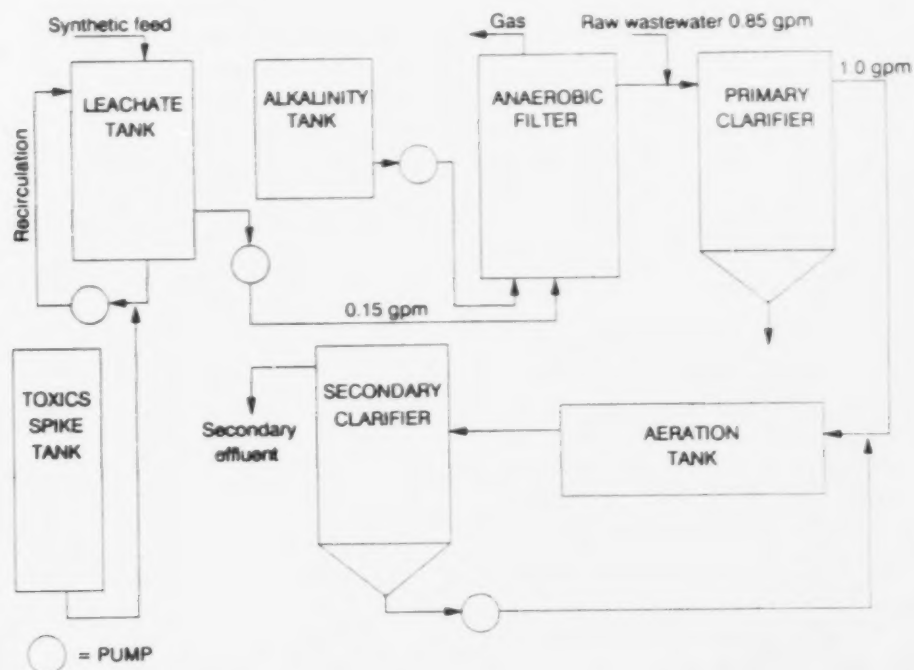


Figure 1. Schematic diagram of anaerobic-aerobic process.

Following an acclimation period of three months, the system was spiked for 12 weeks. Composite aqueous samples were collected during 24-hr periods (such periods are referred to as EVENTS), once every week for six weeks. Samples were analyzed for volatile organic compounds using Method 1624 Revision B (33). Method 1625 Revision B (34) was used to determine semivolatiles. Metals were measured by flame atomic absorption spectrophotometry (35).

While the anaerobic-aerobic system was being built, an anaerobic toxicity assay (ATA) was performed using serum bottles (50 ml culture) to assess potential adverse effects of the selected compounds on the anaerobic process. Acetate enrichment culture was used as the seed organisms.

RESULTS AND DISCUSSION

The results of the ATA showed that the heavy metals did not cause any toxicity to the batch anaerobic acetate enrichment culture in the serum bottles. The organic compounds, however, showed toxicity even at 50% of the design concentrations listed in Table 1. Chloroform appeared to be the most likely cause for the toxicity based on reported inhibition to anaerobic processes (36, 37). The design concentrations of the other organic compounds were not expected to cause toxicity. When the ATA was performed with the individual compounds, only the serum bottles with 5 mg/L or greater concentration of chloroform showed toxicity. Although more work is required to prove that chloroform (5 mg/L or higher) caused toxicity to the anaerobic filter, it was decided to spike the feed to the pilot system with all compounds (in Table 1) except chloroform.

The measured concentrations of volatile leachate compounds are shown in Table 4 for the initial sampling event.

TABLE 4. MEASURED CONCENTRATIONS OF LEACHATE COMPOUNDS (EVENT 1)

LEACHATE COMPOUNDS VOC	CONCENTRATION OF TOXICS (µg/L)									
	LEACH	LEACH (DUP)	FIL EFF	FIL EFF (DUP)	RAW WW	PRI* INF	PRI EFF	SEC EFF	PRI SLU	SEC WAS
Acetone	3625	2906	78.7	94.1	662	575	711	50.7	405	0.0
Methyl ethyl ketone	1388	1166	66.6	76.0	35.8	40.4	104	7.7	33.0	13.7
Methyl isobutyl ketone	446	422	49.9	52.8	11.2	17.0	16.1	4.2	14.6	3.4
Trichloroethylene	144	131	3.2	3.8	1.1	1.4	1.0	0.9	1.2	0.0
Methylene chloride	573	512	105	125	8.3	22.8	16.3	4.8	17.8	9.9
1,1-Dichloroethane	36.8	33.1	7.6	8.2	1.7	2.6	1.8	0.8	2.8	2.4
Chlorobenzene	425	387	337	356	8.9	58.2	37.8	1.6	56.2	4.9
Toluene	843	719	714	774	25.9	129	172	2.0	273	5.0
Ethylbenzene	227	214	116	122	73.8	80.1	108	2.8	103	0.6

LEACH=LEACHATE FIL EFF=FILTER EFFLUENT RAW WW=RAW WASTEWATER PRI EFF=PRIMARY EFFLUENT
SEC EFF=SECONDARY EFFLUENT PRI SLU=PRIMARY SLUDGE SEC WAS=SECONDARY WASTE ACTIVATED SLUDGE

Measured concentrations for duplicate samples were generally in good agreement considering the complex matrices involved. Based on measured flow rates, the masses of volatiles in the influent, effluent, and sludges were calculated. The results of the calculations are shown in Table 5.

TABLE 5. CALCULATED MASS OF LEACHATE COMPOUNDS IN
SLUDGE AND LIQUID PHASES (EVENT 1)

LEACHATE COMPOUNDS VOC	MASS OF TOXICS (gm)									
	LEACH	LEACH (DUP)	FIL EFF	FIL EFF (DUP)	RAW WW	PRI* INF	PRI EFF	SEC EFF	PRI SLU	SEC WAS
Acetone	2.96	2.38	0.064	0.077	3.07	3.13	3.88	0.276	0.087	0.000
Methyl ethyl ketone	1.13	0.953	0.054	0.062	0.166	0.220	0.566	0.042	0.007	0.002
Methyl isobutyl ketone	0.365	0.345	0.041	0.043	0.052	0.092	0.087	0.023	0.003	0.000
Trichloroethylene	0.118	0.107	0.003	0.003	0.005	0.008	0.005	0.005	0.000	0.000
Methylene chloride	0.469	0.419	0.086	0.102	0.038	0.124	0.089	0.026	0.004	0.001
1,1-Dichloroethane	0.030	0.027	0.006	0.007	0.008	0.014	0.010	0.004	0.001	0.000
Chlorobenzene	0.348	0.316	0.276	0.291	0.041	0.317	0.206	0.009	0.012	0.001
Toluene	0.689	0.587	0.584	0.633	0.120	0.704	0.938	0.011	0.059	0.001
Ethylbenzene	0.186	0.175	0.095	0.099	0.342	0.436	0.591	0.016	0.022	0.000

Based on the mass data shown in Table 4, the percent removals were calculated for Event 1. The percent removals obtained for the first event are summarized in Table 6.

TABLE 6. PERCENT REMOVAL OF LEACHATE COMPOUNDS (EVENT 1)

LEACHATE COMPOUNDS VOC	ANAEROBIC		AEROBIC		
	% FILTER REMOVAL	% PRIMARY REMOVAL	% TOTAL REMOVAL	% ADSORBED	% VOLATILIZED, BIODEGRADED, OR CHEMICALLY TRANSFORMED
Acetone	97.4	-23.7	91.2	2.8	88.4
Methyl ethyl ketone	94.4	-157.1	80.9	4.0	77.0
Methyl isobutyl ketone	88.2	5.4	75.5	3.8	71.7
Trichloroethylene	97.4	29.7	36.7	3.3	33.4
Methylene chloride	78.8	28.7	79.0	4.0	74.9
1,1-Dichloroethane	77.4	30.6	71.1	6.4	64.6
Chlorobenzene	14.7	35.0	97.2	4.0	93.2
Toluene	4.7	-33.3	98.5	8.4	90.0
Ethylbenzene	46.1	-35.4	96.4	5.1	91.3

Comparable percent removals were calculated for all sampling events for the volatile organics and results are tabulated in Table 7.

TABLE 7. REMOVAL OF VOLATILE ORGANICS BY ANAEROBIC FILTER

LEACHATE COMPOUNDS	DESIGN FEED CONC $\mu\text{g/L}$	AVERAGE MEASURED FEED CONC $\mu\text{g/L}$	AVERAGE MEASURED FIL EFF $\mu\text{g/L}$	AVERAGE PERCENT FILTER REMOVAL
Acetone	10,000	4,289	78	98
Methyl ethyl ketone	5,000	1,269	69	95
Methyl isobutyl ketone	1,000	355	45	87
Trichloroethylene	400	162	2	99
Methylene chloride	1,200	637	58	91
1,1-Dichloroethane	100	54	11	80
Chlorobenzene	1,100	408	338	17
Toluene	8,000	755	789	-4
Ethylbenzene	600	246	116	55

Except for the aromatic solvents (chlorobenzene, toluene, and ethylbenzene) the removals of VOCs in the anaerobic filter were 80% or higher. Trichloroethylene and acetone showed the highest removals, viz., 99% and 98%, respectively. The design feed concentration shown in Table 7 was not achieved in the feed to the anaerobic filter. This was most likely due to losses of the compounds in the recirculation tank since duplicate samples showed good agreement throughout the study.

Average percent removal of semivolatile compounds by the anaerobic filter were calculated and are presented in Table 8.

TABLE 8. REMOVAL OF SEMIVOLATILE ORGANICS BY ANAEROBIC FILTER

LEACHATE COMPOUNDS	DESIGN FEED CONC $\mu\text{g/L}$	AVERAGE MEASURED FEED CONC $\mu\text{g/L}$	AVERAGE MEASURED FIL EFF $\mu\text{g/L}$	AVERAGE PERCENT FILTER REMOVAL
Dibutyl phthalate	200	38	BDL	---
Bis (2-ethylhexyl) phthalate	100	108	36	67
Nitrobenzene	500	45	BDL	---
Trichlorobenzene	200	161	45	72
Phenol	2,600	1,678	1,105	34

The effluent concentration of dibutyl phthalate and nitrobenzene were below detection limit (BDL). Dibutyl phthalate and bis (2-ethylhexyl)

phthalate were removed by the anaerobic filter. Phenol was not effectively removed by the filter.

Removal of metals was generally high. Table 9 shows the removal achieved by anaerobic treatment.

TABLE 9. REMOVAL OF METALS BY ANAEROBIC FILTER

LEACHATE COMPOUNDS	DESIGN FEED CONC µg/L	AVERAGE MEASURED FEED CONC µg/L	AVERAGE MEASURED FIL EFF µg/L	AVERAGE PERCENT FILTER REMOVAL
METALS				
Aluminum	30,000	3,449	251	93
Copper	100	257	BDL	---
Iron	500,000	253,200	7,941	97
Lead	400	418	20	95
Magnesium	180,000	40,500	32,580	20
Manganese	65,000	20,906	1,860	91
Nickel	1,500	1,647	896	46
Zinc	1,000	597	BDL	---
BDL: BELOW DETECTION LIMIT CONCENTRATION				
---: NOT CALCULATED DUE TO BDL CONCENTRATIONS				

Metal removal in the anaerobic filter is most likely due to chemical precipitation and sorption on the biomass. Since magnesium has high solubility, removal was only 20%.

Removal of volatile organics by the combined anaerobic-aerobic treatment system is presented in Table 10.

TABLE 10. REMOVAL OF VOLATILE ORGANICS BY COMBINED ANAEROBIC-AEROBIC SYSTEM

VOLATILE ORGANICS	AVERAGE REMOVAL	STANDARD DEVIATION
Acetone	94.9	3.4
Methyl ethyl ketone	89.1	5.6
Methyl isobutyl ketone	58.1	19.1
Trichloroethylene	72.9	26.6
Methylene chloride	66.5	13.5
1,1-Dichloroethane	73.6	17.5
Chlorobenzene	93.2	7.6
Toluene	85.4	22.3
Ethylbenzene	92.8	3.5

Total removal was based on the influent to the anaerobic filter and the effluent from the secondary clarifier of the activated sludge system. Chlorobenzene, toluene, and ethylbenzene, which were not efficiently removed by the anaerobic filter, showed 93, 85, and 93 percent removal by the combined anaerobic filter-activated sludge treatment system. Thus, the advantage of the combined process has been demonstrated. The concentrations of semivolatiles and metals in the secondary effluent were too low to calculate the removals for the combined system.

CONCLUSIONS

The combined anaerobic-filter activated sludge treatment system offers advantages for improved treatment of hazardous leachate constituents over either process alone. An anaerobic process ahead of a conventional primary/activated sludge system offers a control technology that can potentially avoid or reduce air emissions due to chlorinated aliphatic solvents and other volatiles which can be anaerobically degraded. Heavy metals at high concentrations did not cause toxicity to the anaerobic filter. Chloroform at 5.0 mg/L was inhibitory to the anaerobic filter. Additional research is needed to define the acceptable level of chloroform that can be tolerated. High removals of most organics was achieved by the anaerobic filter. Total removals by the combined process were also high. The combined system appears to be a feasible process for treatment of hazardous leachates.

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THE EFFECTS OF TEMPERATURE, CONCENTRATION OF SUBSTRATE AND MICROBIAL INOCULUM AND THE SOURCE OF SLUDGE BIOMASS ON THE KINETICS OF BIODEGRADATION

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ABSTRACT

A developed multi-level respirometric protocol is presented for the determination of the biodegradability, microbial acclimation to toxic substrates and first order kinetic parameters of biodegradation and for estimation and quantitation of Monod kinetic parameters (u_m , K and Y) of the toxic organics, in order to correlate the extent and rate of their biodegradation with a predictive model based on chemical properties and structure of those organic pollutant compounds. Respirometric biodegradation kinetic data are provided for representative RCRA alkyl benzenes, phenolic compounds, phthalate esters and ketones and CERCLA leachate organics.

Studies determined the effects of the source of sludge biomass, temperature and concentrations of microbial inoculum and of toxic substrate on the generated biodegradation kinetic parameter data in order to make an assessment of their constancy under a variety of environmental conditions. Sludge biomass from totally domestic, domestic/industrial and fully industrial treatment systems was used in the respirometric study to evaluate the effect of the source of microbiota on the kinetics of biodegradation. Temperatures of 15°C, 25°C, and 35°C were used as culture incubation temperatures and the substrate concentration levels (20, 40, 60, 80 and 100 m/L) were used to determine the effects of temperature and substrate concentration on the kinetic parameter values. Data on the effects of the environmental conditions of the biokinetic parameters for representative toxic organic pollutant compounds are discussed.

A predictive biodegradation structure-activity model based on the group contribution approach was developed with the use of respirometrically generated biodegradation kinetic data. The predictive biodegradation fate model will closely predict the results found experimentally. Fate of structurally related toxic organics may be anticipated without the time and expense of experimental studies.

INTRODUCTION

It has been estimated that 50,000 organic chemicals are commercially produced in the United States and a large number of new organic chemicals are added to production each year (Blackburn and Troxler, 1984). The presence of many of these chemicals in the natural ecosystem is a serious public health problem. The 1986 amendments of Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), known as the Superfund Amendments and Reauthorization Act (SARA) mentioned that cost effective treatments and recycling must be considered as an alternative to the land disposal of wastes. Among the alternative methods available, bioremediation and incineration are the two technologies which destroy the wastes but the cost of bioremediation is estimated to be only about one third the cost of incineration.

Biodegradability and toxicity of organic chemicals determine their behavior in the natural ecosystems and during the treatment of wastewater. The high diversity of species and metabolic efficiency of microorganisms suggests that they play a major role in the ultimate degradation of these chemicals. Microorganisms use these carbon and energy sources for growth, converting them into carbon dioxide, water, ammoniacal nitrogen and new cell material and thus maintain the biological equilibrium in nature. Hence, there is need for data on the biodegradability of organic chemicals to assess their fate in natural ecosystems and in engineered environments. Information regarding the extent and the rate of biodegradation of organic chemicals is very important in evaluating the relative persistence of the chemical in the environment, which in turn is important for regulating its manufacture and use. Thus, there is a need to develop correlations and predictive techniques to assess biodegradability of toxic organics. Lack of an adequate database on biodegradation kinetics has prevented the development of such techniques.

The main objective of this study was to develop a protocol based on oxygen consumption to generate data base on biokinetic constants of representative priority pollutants, RCRA and CERCLA toxic organics. Experiments were conducted using electrolytic respirometry to generate oxygen consumption data from which biokinetic parameters were developed. The representative compounds included 20 benzenes, 7 phthalates, 5 polycyclic aromatic hydrocarbons, 4 nitrosoamines, 8 phenols, 4 ketones, p-nitroaniline and benzyl alcohol with aniline as the reference compound.

The environmental factors investigated were temperature, concentration of biomass and substrate and the source of biomass. These effects on biodegradation kinetic rates will subsequently be related to the structural properties of the compound. This in turn will facilitate prediction of the extent and rate of biodegradation of organic pollutant chemicals from the knowledge of their structural properties. The specific organic compounds, used for the study of the effects of environmental factors on kinetic parameters were: benzene, toluene, ethylbenzene, phenol, resorcinol, 2,4-dimethyl phenol, dimethyl phthalate, diethyl phthalate, butyl phthalate and butyl benzyl phthalate.

BACKGROUND

An extensive review on the use of oxygen consumption measurements in routine examination of sewage, in control of sewage treatment processes and in the application to specific wastes or compounds has been presented by Jenkins (1960), Montgomery (1967) and King and Dutka (1986). Techniques used to evaluate biodegradation kinetics were reviewed in detail by Howard, *et al.* (1975, 1981) and Grady (1985). These techniques utilize continuous, fed-batch and batch type reactors for providing data from which kinetic parameters can be evaluated.

The success of batch techniques in obtaining intrinsic kinetic parameters (dependent only on the nature of the compound and the degrading microbial community and not on the reactor system used) was indicated in the studies of Simkins and Alexander (1984, 1985), Robinson and Tiedje (1983), Cech *et al.* (1984), Braha and Hafner (1987), Tabak, *et al.* (1984), Larson and Perry (1981) and Paris and Rogers (1986).

Measurement of oxygen consumption through electrolytic respirometry is a batch type technique which has been shown to be very promising for automating data collection associated with biodegradation and intrinsic kinetic parameters. Studies performed by Dojlido (7), Larson and Perry (22), Tabak *et al.* (34), Oshima *et al.* (27), Gaudy *et al.* (9, 10) and Grady *et al.* (13, 14, 15) have utilized the electrolytic respirometry approach to generate biodegradation kinetic data.

Dojlido (7) divided the oxygen uptake curve into seven different phases and then proposed an empirical model for each phase and evaluated the biodegradability and toxicity of a test compound by measuring empirical rate constants and time interval associated with each phase. Various phases were distinguished by identifying inflection points in the curve through the plots of the logarithm of the slope versus time.

Tabak *et al.* (34) and Oshima *et al.* (27) sought to capitalize on Dojlido's method of identifying inflection points in order to quantify more fundamental rate coefficients. In order to identify more fundamental (and, therefore, intrinsic) kinetic coefficients, they used the generalized concept of oxygen uptake by Gaudy and Gaudy (8). Substrate removal was divided into exponential and declining phases separated by an inflection point, and the endogenous phase. They coupled substrate removal and cell growth to oxygen consumption by imposition of an electron balance and consequently were able to evaluate μ_m from oxygen consumption data up to the inflection point. They proposed the use of the lag time as an indicator of how difficult it is to achieve acclimation to a test compound and their respirometric studies were carried out with an unacclimated biomass.

The justification for using respirometry to obtain intrinsic kinetic coefficients lies in the concept of oxygen consumption as an energy balance [Busch *et al.* (4); Gaudy and Gaudy (8)]. This concept states that all of the electrons available in a substrate undergoing biodegradation must either be transferred to the terminal acceptor or be incorporated into new biomass or soluble microbial products. If the concentrations of the substrate, the

products and the biomass are all expressed in units of chemical oxygen demand (COD), then the oxygen uptake can be calculated in a batch reactor from an equation relating oxygen uptake to substrate, biomass and soluble products [Grady et al. (13)]. Furthermore, since biomass growth and product formation are proportional to substrate removal, this suggests that an oxygen uptake curve can provide the same information as either a substrate removal curve or a biomass growth curve. This latter concept has recently been used by Gaudy et al. (12, 14) to calculate biodegradation kinetics. Specific growth rates obtained from growth studies as slopes of plots of $\ln$ (biomass concentration) or $\ln(X)$ versus time at different substrate concentrations, compared favorably with those obtained from exponential phase of respirometric oxygen uptake curves as slopes of plots of $\ln$ (d oxygen uptake/d time or $\ln (dO_2/dt)$ versus time.

Studies of Grady et al. (12, 14) have demonstrated that it is possible to determine intrinsic kinetics of single organic compounds by using only measurements of oxygen consumption in respirometric batch reactors. With the use of computer simulation techniques and non-linear curve fitting methods, intrinsic kinetic parameters were obtained from oxygen consumption data and were shown to be in agreement with those obtained from traditional measurement of substrate removal (DOC, SCOD, ^{14}C) or cell growth.

MATERIALS AND METHODS

EXPERIMENTAL APPROACH

Electrolytic Respirometry

The electrolytic respirometry studies were conducted using an automated continuous oxygen uptake and BOD measuring Voith Sapromat B-12 (12-unit system) electrolytic respirometer-analyzer.

The nutrient solution used in these studies was an OECD synthetic medium (OECD Guidelines for Testing of chemicals, OECD, Paris, France, 1981) consisting of measured amounts per liter of deionized distilled water of (1) mineral salts solution; (2) trace salts solution, and (3) a solution (150 mg/L) of yeast extract as a substitute for vitamin solution.

A comprehensive description of the procedural steps of the respirometric tests and of the experimental design employing test and control systems is presented elsewhere [OECD Guidelines for Testing of Chemicals (1983), Tabak et al. (1984)].

For fully automatic data acquisition, frequent recording and storage of large numbers of oxygen uptake data, the Sapromat B-12 recorders are interfaced to an IBM-AT computer via the Metrabyte interface system. The use of a Laboratory Handbook software package allows the collection of data at 15 minute intervals.

Determination of Substrate Biodegradability from Oxygen Uptake Data

In this study, biodegradation was measured by three approaches: the first, as the ratio of the measured BOD values in mg/L (oxygen uptake values of test compound minus inoculum control - endogenous oxygen uptake values) to the theoretical oxygen demand (ThOD) of substrate as a percent; the second as a percentage reduction of the original amount of test compound as measured by dissolved organic carbon (DOC) changes [OECD Guidelines for Testing of Chemicals (Method DGXI 283/82, Revision 5) (26)]; and the third, as a percentage reduction of the original amount of test compound as measured by specific substrate analysis.

Graphical representation of percent biodegradation based on the BOD/ThOD ratio were developed against time for each test compound. The experimental DOC data for the initial samples and samples from reaction flasks collected at the end of experimental run were used to calculate the percent biodegradation based on the percent of DOC removal in the culture system.

Determination of Kinetic Parameters of Biodegradation

The Monod equation, relating cell growth to biomass and substrate concentration and the linear law, relating cell growth to substrate removal are the most popular kinetic expressions which can provide adequate description of growth behavior during biodegradation of substrate. The Monod relation states that cell growth is first order with respect to biomass concentration (X) and mixed order with respect to substrate concentration (S) by the equation

$$dX/dt = (\mu_m X)/(K_s + S) \quad (1)$$

Cell growth is related to substrate removal by the linear law by the equation

$$dX/dt = -Y(dS/dt) \quad (2)$$

The kinetics of biodegradation were evaluated by quantifying μ_m , K_s and Y kinetic parameters expressed in the equation for the rate of substrate removal, r_s :

$$r_s = -\mu_m X/Y \quad (3)$$

where X is the concentration of biomass capable of utilizing the organic substrate and Y is the biomass yield coefficient for the compound and in the Monod equation:

$$\mu = \mu_m S_s/(K_s + S_s) \quad (4)$$

(if the compound is not inhibitory to its own biodegradation) or by the Haldane equation:

$$\mu = \mu_m S_s / K_s + S_s + (S_s^2 / K_i) \quad (5)$$

if the compound is inhibitory. In these equations, μ_m is the maximum specific growth rate, K_s is the half saturation coefficient, K_i is the inhibition coefficient and S is the concentration of substrate.

Determination of Rates of Exponential and Declining Growth

The first order kinetic rate constants (specific growth rate parameters) were determined by the linearization of the BOD curves or transforming the typical BOD curve to the linear function of time t , by the relationship of $\log dO_u/dt$ to t , which gives straight lines expressing the exponential and declining endogenous phases of the BOD curve. The slope of the $\ln(d \text{ oxygen uptake}/dt)$ versus t give specific rate constants of the exponential growth phase (μ values) and the declining growth phase (μ' values) of the BOD curve as described by Dojlido (7), Tabak et al. (34), Oshima et al. (27), and Tabak et al. (35, 36).

Acclimation time values (t_0) and the time values for the initiation and termination of the declining growth phase (t_1 and t_2) for each test compound were determined from linearized expressions of BOD curves.

Estimation of Monod Kinetic Parameters

Based on the concept of oxygen uptake as energy balance (Gaudy and Gaudy, 1971), if the concentrations of the substrate, the products and the biomass are all expressed in BOD units, then the oxygen uptake (O_u at any time in the batch reactor may be calculated [Grady et al. (13)] from

$$O_u = (S_{s0} - S_s) - (X - X_0) - (S_p - S_{p0}) \quad (6)$$

where S_{s0} , S_{p0} and X_0 are the concentrations of substrate, products and cells, respectively, at time zero, and S_s and S_p are the concentrations of substrate and product, respectively, at time t .

To apply equation (4) for the determination of kinetic coefficients, equations must be available which express the concentrations of soluble substrate (S_s), soluble product (S_p) and biomass (X) as functions of time. For batch reactors, those equations are:

$$dS_s/dt = -(\mu_m/Y)S_sX/(K_s + S_s) \quad (7)$$

$$dS_p/dt = Y_p(-dS/dt) = (Y_p\mu_m/Y)S_sX/(K_s + S_s) \quad (8)$$

$$dX/dt = \mu_m S_s X / (K_s + S_s) - K_s b X / (K_s + S_s) \quad (9)$$

where S_s = soluble substrate concentration; S_p = soluble product concentration; Y_p = product yield; and b = decay coefficient.

In equation (9) the effect of decay is negligible when the substrate concentration is high, but as substrate concentration decreases, the importance of the decay term increases and, finally, when substrate concentration approaches zero, the decay term approaches traditional first order rate.

Equations (7), (8) and (9) are solved simultaneously and the values of substrate, biomass and product concentrations obtained over time are substituted in equation (6) to calculate theoretical oxygen uptake.

A. Determination of Y Constant

The initial estimate of yield coefficient, Y can be obtained by identifying the start of the plateau, which is the point at which substrate concentration is approximately equal to zero. Using equations (2) and (8), equation (6) can be expressed as

$$\begin{aligned} O_u &= (S_o - S) - Y(S_o - S) - Y_p(S_o - S) \\ &= (1 - Y - Y_p)(S_o - S) \end{aligned} \quad (10)$$

At the plateau the substrate concentration is very low compared to S_o , so that it can be neglected. This simplifies equation (10) and on rearranging this simplified equation becomes:

$$Y = (S_o - O_{upt})/S_o - Y_p \quad (11)$$

Where O_{upt} is the cumulative oxygen uptake value at the initiation of plateau, S_o is the concentration of substrate at time zero, and Y_p is the product yield coefficient. Y constant can then be estimated from equation (11).

A vertical line is drawn at the point of intersection of the tangents of the exponential and plateau phases of the curve. The oxygen uptake value obtained at the point of intersection of the vertical line (drawn through intersection of tangents) and oxygen uptake curve is the O_{upt} value - [cumulative oxygen uptake value at the initiation of plateau].

The O_{upt} value is then substituted into equation (11), for Y determination. Y_p is soluble product concentration formed, divided by initial substrate concentration. In this study, product yield (Y_p) was negligible.

B. Determination of μ_m Constant

The initial estimate of μ_m is obtained by assuming that $S \gg K_s$ in equation (1) which simplifies this equation. Integrating this simplified equation

$$X = X_0 \exp(\mu_m t) \quad (12)$$

Using equation (2) substitute S in terms of X in equation (6) (with S_p and S_{p0} both equal to zero) and then rearranging

$$X = [O_u / (1/Y - 1)] + X_0 \quad (13)$$

Substituting equation (12) in equation (13), and taking natural log gives an expression from which μ_m can be estimated.

$$\ln [X_0 + O_u / (1/Y - 1)] = \ln X_0 + \mu_m t \quad (14)$$

A plot of $\ln[X_0 + O_u / (1/Y - 1)]$ versus time, t , will give a straight line with slope μ_m .

μ_m - the maximum specific growth rate can be determined from experimental oxygen uptake curve plot in the following manner:

- (1) Values of the change of O_u with time (dO_u/dt) or slopes are determined along the entire experimental oxygen uptake curve.
- (2) These dO_u/dt (slope) values are then plotted against the cumulative O_u values for each time interval.
- (3) The slope of the developed linearized form of oxygen uptake curve is the estimated μ_m value.

C. Determination of K_s Constant

The oxygen uptake value O_{ut} associated with $1/2$ of the estimate of u_m is used in equation

$$S = S_0 - O_{ut}/(1 - Y - Y_p) = K_s \quad (15)$$

to get an initial estimate of K_s . The major impact of K_s is upon the shape of the oxygen uptake curve in the region of the plateau. Comparison of the experimental curves to a family of standardized curves as an initial estimate provides an initial estimate of K_s that is sufficient for non-linear curve fitting techniques for quantitation of the kinetic parameters.

K_s - the half saturation constant or the substrate concentration at which the specific growth rate is 1/2 the maximum specific growth rate can be obtained from the experimental oxygen uptake curve, as described by Tabak et al. (1989).

D. Determination of b Coefficient

The importance of decay coefficient, b , increases only when substrate concentration becomes too low to support biomass growth. This implies that the major effect of decay on the oxygen uptake curve is when the plateau is reached. At this point, since S_s is assumed to be zero, then the first term in equation (9) approaches zero and the equation simplifies to

$$dX/dt = -bX \quad (16)$$

The decay coefficient is obtained by nonlinear curve fitting of equation (16) to the oxygen uptake data after the plateau is reached.

E. Determination of Y_p Coefficient

The product yield, Y_p is estimated by dividing the residual product concentration at the plateau by the initial substrate concentration, S_0 .

Quantitation of Monod Kinetic Parameters

The methodology for quantitation of the Monod kinetic parameters requires the use of the above specific methods for estimating them initially and subsequently followed by computer simulation methods coupled with non-linear curve fitting techniques and is based on the use of measured values of initial growth and growth yield. The method requires the use of the kinetic equation relating growth rate of biomass in presence of substrate, the substrate utilization rate, product formation rate and rate of oxygen consumption from O_2 uptake (BOD) curves to calculate and use the theoretical oxygen consumption data to quantitate the biokinetic parameters.

The determination of the kinetic parameters associated with biodegradation requires a series of steps. The initial substrate (S_{s0}) and

biomass (X_0) concentration must be carefully measured in COD units. The ratio of the two values must lie in a certain range in order to allow independent evaluation of μ_m , K_s and Y [Simkins and Alexander (30, 31)]. Grady's studies (12, 13) have shown that a S_{∞}/X_0 ratio of around 20 works well. The value of Y_p may be estimated by determining the residual stable SCOD concentration after substrate depletion (plateau area). It is numerically equal to the residual SCOD divided by the initial SCOD. The value of the decay coefficient, b , may be determined by fitting to the oxygen consumption curve after the plateau when the only activity contributing to oxygen consumption is endogenous metabolism and cell decay. Once X_0 , S_{∞} , Y_p and b are known, μ_m , K_s and Y may be determined by non-linear curve fitting techniques [Grady (12, 13, 14)]. Assuming a set of values for μ_m , K_s and Y , theoretical oxygen uptake is calculated using equations (6) - (9). The error between the theoretical and the actual oxygen uptake curve is calculated and then used to obtain new estimates. The procedure is repeated until minimum error is found.

The technique involves the calculation of a theoretical oxygen consumption using oxygen uptake equation (6) and equations for substrate, product and biomass concentrations (7) - (9) with assumed Monod parameters. The residual sum of squared errors (RSSE) associated with the difference in calculated and experimental oxygen uptake values is used to obtain new estimates. The above procedure is repeated until a minimum RSSE is found.

The Grid Search technique was selected as a most suitable non-linear curve fitting technique for application in the determination of the kinetic parameters from oxygen uptake data, because it can allow easy discrimination between local minima and the global minimum RSSE. This technique enables a comparison between the calculated and experimental oxygen uptake data. The value of Y is fixed. For this value of Y , a pair of μ_m and K_s which give RSSE is found on a $\mu_m:K_s$ plane. The above procedure is repeated with other values of Y . Values of μ_m , K_s and Y which give minimum RSSE associated with the difference in calculated and experimental oxygen uptake data constitute the best values of the kinetic parameters.

The values of μ_m , K_s and Y developed from grid search technique, which when substituted into equations (7) - (9), will provide X and S values, which (when substituted into oxygen uptake equation 4) will in turn provide calculated oxygen uptake values at the region of the plateau, closest to the experimental oxygen uptake values, with a minimum RSSE, will constitute the best quantitative kinetic parameter values.

A more comprehensive description of the procedural steps in the determination of rates of exponential and declining growth as well as in the estimation and quantitation of Monod kinetic parameters for toxic organic compounds from oxygen consumption data has been given elsewhere by Tabak et al. (1989a, b, c).

Modifications for Volatile and Sparingly Soluble Compounds

Volatile Compounds--

The equations (7) - (9) are valid for a non-volatile compound present at a concentration below its solubility limit, so they have to be modified for volatile and sparingly soluble compounds. The respirometer reactors being sealed, when compound is added it partitions itself between gas and liquid phases. As biodegradation proceeds and the substrate concentration decreases in liquid phase, it is transferred from the gas phase to the liquid phase to maintain equilibrium in accordance with Henry's law. If S is the total substrate concentration in the system, S_L is the substrate concentration in the liquid phase, and V_g and V_L are volumes of gas and liquid phases respectively, then

$$S_L = S / (1 + HV_g/V_L) \quad (17)$$

where H is the dimensionless Henry's Law Constant, specified by the following equation

$$H = \frac{[\text{Henry's Law Constant in atm/moles/m}^3]}{RT} \quad (18)$$

R is the universal gas constant and T is the temperature in $^{\circ}\text{K}$.

Equation 17 was derived to quantify the partitioning between the gas and liquid phases. The use of Henry's Law Constant is justified since the molar concentration of the compound is approximately 10^{-4} , and hence the activity coefficient in the liquid phase is equal to 1.0.

Let S_{L1} = concentration of substrate in liquid phase at time t_1

S_{L2} = concentration of substrate in liquid phase at time t_2

then using equation (7)

$$S_{L2} = S_{L1} - [(\mu_m S_{L1} X_{t1}/Y)dt / (K_s + S_{L1})] + (S_{L1} - S_{L2})(HV_g/V_L)$$

As dt tends to zero the above equation results in

$$dS_L/dt = - (\mu_m S_L X/Y) / [(K_s + S_L)(1 + HV_g/V_L)] \quad (19)$$

Substituting equation (17) in equation (19)

$$dS/dt = - (\mu_m SX/Y)/(K_s' + S) \quad (20)$$

where $K_s' = K_s(1 + HV_g/V_L)$. Similarly equations (8) and (9) change to

$$dS_p/dt = (Y_p \mu_m SX/Y)/(K_s' + S) \quad (21)$$

$$dX/dt = [(\mu_m SX)/(K_s' + S)] - [(K_s' bX)/(K_s' + S)] \quad (22)$$

Sparingly Soluble Compounds--

A sparingly soluble compound will dissolve into the solution phase up to its solubility limit and the undissolved part will exist as a different phase. As the compound undergoes biodegradation in solution phase more of the undissolved part dissolves into the solution, keeping its concentration in solution phase constant at the solubility limit. Therefore, degradation proceeds at a constant substrate concentration as long as total substrate concentration in the system is greater than its solubility limit. Now, if the compound is also volatile then depending on Henry's law constant it will partition itself into the gas phase and liquid phase. When the microorganisms degrade this compound from the solution phase, then compound from the undissolved part dissolves into solution phase. This keeps the compound concentration in the solution phase and gas phase constant. If S is the total substrate concentration (per unit volume of liquid phase) in the system and S_s is its solubility limit then the concentration in solution phase and gas phase will be constant as long as $S > S_s(1 + HV_g/V_L)$. So if substrate concentration is held constant at S_s in equations (7), (8) and (9) then they can be solved analytically and the solutions are

$$X = X_0 \exp[(\mu_m S_s - bK_s)t/(K_s + S_s)] \quad (23)$$

$$S = S_0 - [(\mu_m S_s/Y)/(\mu_m S_s - bK_s)](X - X_0) \quad (24)$$

$$S_p = [(Y_p \mu_m S_s/Y)/(\mu_m S_s - bK_s)](X - X_0) \quad (25)$$

Thus, equations (23), (24) and (25) should be used when the total concentration of the substrate, S is greater than $S_s(1 + HV_g/V_L)$ and equations (20), (21) and (22) should be used when the total substrate concentration, S is less than or equal to $S_s(1 + HV_g/V_L)$.

RESULTS AND DISCUSSION

Respirometric biodegradability, biokinetic and Monod kinetic data for selected RCRA alkyl benzenes, phenols, phthalates and ketones were generated in these studies. The electrolytic respirometry oxygen uptake data for the test compounds, the control reference compound aniline, the inhibition and endogenous control systems were generated revealing the lag phase (acclimation phase), the biodegradation (exponential) phase, the different bio-reaction rate slopes (characteristic of the test compound) as well as the plateau region at which the biooxidation rate reaches that of the endogenous rate of microbial activity.

According to the OECD interpretation of biodegradation (BOD) data, test compounds were judged to be easily biodegradable if they showed a high level of oxygen uptake within 10 days after the observed level of biodegradation first exceeds 10 percent (the time at which 10 percent biodegradation is achieved is considered the lag or acclimation period). In addition, the results of biodegradation are valid if the control reference substrate, aniline achieved 60 percent biodegradation within a period of 28 days.

Based on the biokinetic equations relating growth rate of microbiota in presence of above compounds, the substrate utilization rate, and rate of oxygen uptake (BOD) curves, specific growth rate kinetic parameters (biodegradation rate constants) were derived as slope values of the linearized plots (plots of the log of dO_2/dt) of exponential and declining growth phases of the BOD curve. The acclimation time values (t_0), and time values for the initiation and the termination of the declining growth phases (t_1 and t_2) for the test compounds and aniline were also generated.

The estimations of the Monod kinetic constants for benzene, phenol, phthalate, and ketone compounds were determined directly from experimental oxygen uptake curves without the consideration of initial growth and growth yield assumption.

Subsequently the Monod kinetic constants were quantitated with the use of computer simulation methods coupled with a non-linear regression technique (Grid Search Method). The values of μ_m , K_s and Y were developed from this technique with the use of oxygen uptake equation and equations for substrate, product and biomass concentration and through a comparison of experimental and theoretical (calculated) oxygen uptake curves, with a minimum RSEE value associated with them.

The biodegradation of alkyl benzenes, phenols, phthalates and ketones and the reference compound, aniline at 100 mg/L concentration levels in synthetic medium containing 30 mg/L sludge biomass (dry weight basis) was measured with the use of oxygen consumption values and the ratios of BOD values to the theoretical oxygen demand (ThOD) of substrate. The oxygen uptake data were generated over a period of 20-40 days.

The oxygen uptake rate revealed that all of them were biodegradable at the concentration level of 100 mg/L and under the experimental conditions used

and according to OECD interpretation of biodegradability of the compounds under such environmental conditions.

QUANTITATION OF MONOD KINETIC CONSTANTS

Table 1 summarizes the quantitative kinetic parameter values for the alkyl benzenes, phenols, phthalates and ketones and for aniline and provides the average percent error values between the experimental oxygen consumption values and the theoretical (calculated) oxygen uptake data (derived from best fit parameter values). The average percent error between the experimental and calculated oxygen uptake data was calculated by

$$\text{Absolute Value of } [(100/n) \sum ((O_u)_e - (O_u)_p)/(O_u)_e]$$

where 'e' and 'p' denotes experimental and predicted values respectively. The biokinetic constants for volatile and non-volatile compounds were calculated using equations (19) - (22). For sparingly soluble compounds equations (23) - (25) were used until the total concentration was greater than modified solubility limit and equations (19) - (22) used thereafter.

The values of biokinetic constants given in Table 1 are the average of two replicates except for aniline, which had eight replicates, so for aniline the standard deviation is given along with the mean values. The representative oxygen uptake curves are given in Figures 1-4, which illustrate the agreement between the experimental (asterisks) and the calculated (solid lines) data. The three biokinetic constants have major impacts on different parts of the curve. The maximum specific rate constant μ_m , affects the exponential part of the curve and examination of data sets revealed that generally good agreement was obtained in this region. The oxygen uptake at the plateau is affected mainly by the yield coefficient Y . The predicted curves agreed well with experimental curves at this point, so one could be confident about yield values. The half saturation constant K_s , defines the shape of the curve before the plateau. The agreement in this region was not very good for all the test compounds, so one would tend to be less confident about the values of K_s .

The variability of oxygen uptake data between replicates of the compounds is typical for biodegradation of toxic compounds (Urano and Kato, 1986; Grady, et al., 1989 and Gaudy, et al., 1988) and this appears to be inherent in the use of natural microbiota (Grady and Lim, 1980). Even for the same compound, different patterns of oxygen uptake have been observed several times throughout this study as seen in Figures 1-4.

EFFECT OF DIFFERENT ENVIRONMENTAL PARAMETERS ON RATE CONSTANTS

To study the effects of different parameters; temperature, concentration (substrate as well as biomass) and source of biomass, 10 compounds were selected from the list of 32 which were biodegraded. The criteria for selection was that they had to be present in at least three of the four USEPA lists; RCRA list, Superfund list, Priority pollutant list and Best

Demonstrated Available Technology (BDAT). The ten compounds selected based on these criteria were benzene, toluene, ethyl benzene, phenol, resorcinol, 2,4-dimethyl phenol, dimethyl-, diethyl-, dibutyl- and butyl-benzyl phthalates.

A statistical analysis was performed to find whether a kinetic rate constant was similar or different under various treatments for each parameter (Walpole and Myers, 1972). One way analysis of variance (ANOVA) was used for this purpose. The theory for one way ANOVA assumes that various treatments have a common variance. Hence, Cochran's test was used to check the equality of variances for different treatments. The value of f , which is the value of the random variable F having the F distribution was calculated and compared with the critical value at 95 percent confidence level, denoted by the variable F . If the value of f was less than the critical value, F , then the hypothesis that the kinetic parameters under all treatments are equal is valid. The Cochran's equality of variance test, requires the calculation for the parameter g and comparing its value with the critical value G at 95 percent confidence level (Walpole and Myers, 1972).

Effect of Substrate Concentration

The experiments were conducted at 25°C and at substrate concentrations of 20, 40, 60, 80 and 100 mg/L, using sludge from Little Miami wastewater treatment plant (Cincinnati) as inoculum. The duration of each of the experiment was about 20 days. Duplicate runs were made for each of the five concentrations for all the compounds. The results of these experiments are presented in Table 2. In Table 2 F and G are critical values and f and g are calculated values at 95% confidence level for ANOVA and Cochran's test of equality of variances.

The F -test showed that μ_m values are similar at all the concentration levels for all the compounds. This suggests that μ_m is independent of initial substrate concentration. Similar trends have been confirmed for ethylene dibromide, aniline and *m*-nitro phenol (Aelion, et al., 1989), at low concentrations of phenol (Scott, et al., 1983) and for phthalates and polyaromatics (Grady, et al., 1989a). Fannin, et al. (1981) reported that the degradation rate decreased with increase in concentration for phenol. They studied phenol degradation in the concentration range 100-400 mg/L and phenol is inhibitory to microbial degradation beyond 100 mg/L (Grady, et al., 1989), so degradation rate decreases with increasing concentration beyond 100 mg/L. Variation in lag time is not more than one day for a substrate concentration range of 20 -100 mg/L, which indicates that at least in this concentration range lag time is independent of substrate concentration.

Effect of Biomass Concentration

The experiments were carried out at 25°C, with a substrate concentration of 100 mg/L and biomass concentrations of 20, 30 and 40 mg/L. Activated sludge from the Little Miami wastewater treatment plant (Cincinnati) was used as inoculum. The duration of experiments was 10-20 days. Experiments were done using duplicates for all the compounds at each concentration level of biomass.

The results of these experiments are presented in Table 3 along with the statistical analysis.

The F-tests shows that the specific rate constant μ_m , is independent of initial biomass concentration. Aichinger (1989) has found a similar trend for phthalates and polyaromatic hydrocarbons. He has used a method similar to the one used in this study to estimate kinetic parameters from oxygen uptake data. Fannin, et al. (1981) and Nabivanets, et al. (1975) reported that increasing the amount of bacterial inoculum caused a significant linear increase in the degradation rate. They had calculated the rate by dividing percentage degraded by time period (%/hr). This was the simple approach of calculating the rate without taking the biomass concentration into account. Their findings could be explained simply: when larger bacterial populations are initially present in the inoculum, faster substrate consumption would result. As shown in Table 3 there is a distinct decrease in lag time with an increase in initial biomass concentration for all the compounds except phthalates, which may be due to the presence of a larger number of microorganisms at the start of the experiment.

Effect of temperature

To study the effect of temperature, experiments were carried out at substrate concentration of 100 mg/L and at three different temperatures 15°, 25° and 35°C, using activated sludge from the Little Miami wastewater treatment plant (Cincinnati) as inoculum. The duration of experiments was 10-20 days. Experiments were conducted with duplicate samples of all the compounds at each temperature. Microorganisms were not acclimated to the temperature of 15° or 35°C before the start of the experiment. The results of these experiments are presented in Table 4. At 15°C benzene, toluene and ethyl benzene were not mineralized completely at the cessation of oxygen consumption. The residual material were probably the transformation products, although no studies were done to identify them. These products may have been inhibitory to further degradation of three benzenes.

The maximum specific rate constants for all the compounds increased with an increase in temperature over a temperature span of 15°-35°C. The effect of temperature on the rate constant was described by the Arrhenius equation

$$\mu_m = A \exp(-E/RT)$$

where	A	-	frequency factor (hr ⁻¹)
	E	-	activation energy (cal/mol)
	R	-	gas constant (1.986 cal/°K x g mole)
	T	-	absolute temperature (°K)

Arrhenius plot of the temperature data showed good agreement for different compounds (Figure 5). Table 4 lists the frequency factor and the activation energy of some of the test compounds. These activation energies of test compounds except for phenol and diethyl phthalate are in the range reported for ordinary enzyme reactions and they indicate that the degradation of these compounds in wastewater treatment plant is not thermodynamically hampered (Larson, et al., 1981). Several researchers have reported that degradation rates are directly proportional to temperatures (Johnson and Heitkamp, 1984; Hollis, 1976 and Stephenson, et al., 1983). Furthermore, the results in Table 4 indicate that lag time decreases with increase in temperature.

Effect of Sludge Source

The experiments were conducted with sludges from four different sources; Little Miami wastewater treatment plant (Cincinnati), Test and Evaluation Facility of USEPA (Cincinnati), Monsanto plant (Addyston, OH) and BP America plant (Lima, OH). The substrate and biomass concentration used was 100 and 30 mg/L respectively. Duplicate samples were run for all the compounds with sludge from each source. The results of the experiments are given in Table 5.

Statistical analysis showed that the kinetic constants obtained with sludges from domestic, domestic-industrial and industrial sludge sources were, except for a few exceptions, in fairly good agreement and were shown to fall within a similar range as far as microbial activities are concerned. In this study correlations were made between microbial populations representing domestic and industrial waste treatment sludge, and exceptions will occur which could suggest that kinetic constant may be unique to the biomass representing some particular industrial waste treatment system. In such exceptions, the history and composition of microbial community may play an important role in the rate of biodegradation but the extent of biodegradation does not depend on the culture used. Data, however, support that in most cases, there was a fair correlation between specific rate constant for any compound biodegraded by microbiota from different sources of sludge, and that the extent of biodegradation (% biodegraded) for all the test compounds) was similar. An even better correlation between kinetic constants were observed in studies (not reported here) relating sludges from different domestic waste treatment systems only (studies *in progress*).

These data corroborate the work of Lewandowski (1988) on POTW treatment of industrial organic wastes. His experimental data suggest an unexpected capacity of microorganisms from a domestic treatment plant (Livingston) to degrade chlorinated hydrocarbons (2-chlorophenol, 2,6-dichlorophenol, and 2,4-D) at rates that were virtually the same as those for the plant handling industrial waste (PVSC). Even the phenol degradation rates were the same, although PVSC had experienced significant prior exposure. In addition, the dominant microbial populations were also very similar, both before and after phenolic exposure. Since the operational characteristics for these two plants are very different, these results raise the possibility that plant-to-plant differences in response to hazardous wastes may not be as severe as some have imagined.

Microbial adaption to the compounds tested was quite rapid, resulting in a 2- to 5-fold increase in the average degradation rates after only the second exposure in a batch reactor. When multiple substrates were tested, the individual compound degradation rates in the mixture were very similar to the degradation rates as sole carbon source.

CONCLUSIONS

Electrolytic respirometry approach involving natural sewage, sludge and soil microbiota is a very successful, accurate, cost effective and less labor intensive method for generating biodegradability/ inhibition and biokinetic data. This procedure measures the biodegradability and determines the intrinsic kinetic parameters of biodegradation by using measurements of oxygen consumption in respirometric batch reactors and by applying non-linear curve fitting techniques to oxygen uptake data. The method is very promising for automating data collection associated with biodegradation and the intrinsic kinetic parameters. The values of the kinetic parameters for single organic compounds in synthetic media determined from oxygen consumption data are similar to those obtained from traditional measurement of substrate removal (DOC, SCOD, ^{14}C) or cell growth thus can be used for the assessment of the biodegradative fate of toxic organics in waste treatment systems.

The electrolytic respirometry, with its automatic collection of data, is a simple and reliable method to study biodegradation of toxic compounds, including slightly soluble and volatile compounds. Experiments were conducted for 56 organic compounds with aniline as the reference compound. The results showed that 32 compounds degraded under the experimental conditions and for these compounds Monod parameters were calculated. The course of biodegradation of volatile and slightly soluble compounds could be modeled with the Monod model.

Experiments were also conducted to study the effect of temperature, substrate concentration, biomass concentration and source of sludge on the kinetic rate constant. The rate constant increased with increase in temperature and was described by the Arrhenius equation. It proved to be independent of the initial substrate and biomass concentration used. The kinetic constants are not usually dependant on history and composition of microbial community but there are a substantial number of exceptions. The extent of biodegradation does not depend on the culture used.

Wiggins, et al. (1987) and Ventullo and Larson (1986) had suggested that lag time in aquatic systems may reflect the time for multiplication of the initially small population of active organisms to a critical level and increased activity per cell. If growth of a small degrading population to significant levels account for the observed adaptation response, then at higher concentration one might expect more rapid growth and therefore reduced lag periods. In this study it was found that in the concentration range of 20-100 mg/L, lag time proved to be independent of substrate concentration and it decreased with increase in initial biomass concentration, which supports the above hypothesis.

Developed biokinetic data, unaffected by the varying environmental conditions, will enable ultimate determination of the fate of organic compounds of similar molecular structure to those experimentally studied by way of the established predictive treatability models based on structure/activity relationships. A possible relationship between the kinetic parameters and the effect of different factors on these parameters and the structural properties of toxic organics can facilitate prediction of the extent and rate of biodegradation in wastewater treatment systems.

A biodegradation kinetic data base will enable the classification of biodegradability and the inhibitory effects on the sludge biomass of the toxic organic RCRA and CERCLA pollutant compounds. The biokinetic data will provide the basic pilot and full scale treatability information and an accurate assessment of the need for pretreatment for these toxic pollutants.

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TABLE 1. QUANTITATIVE MONOD KINETIC PARAMETER VALUES

Compound	μ_m (hr ⁻¹)	K_s mg/L	r mg/mg	Avg. % error
Aniline	0.253± 0.015	28.93± 2.51	0.43± 0.05	5.2±2.4
Benzolates				
Benzene	0.282	6.57	0.27	5.32
Ethyl benzene	0.218	10.07	0.34	8.77
Toluene	0.523	7.75	0.36	5.62
o-Xylene	0.123	0.75	0.26	12.94
m-Xylene	0.140	2.47	0.38	13.43
p-Xylene	0.194	10.03	0.23	19.21
Cumene	0.109	10.00	0.23	18.29
Butyl benzene	0.110	10.00	0.82	0.32
sec-Butyl benzene	0.021	10.00	0.22	18.91
tert-Butyl benzene	0.135	7.47	0.53	8.52
1-Phenyl hexane				
Phthalates				
Dimethyl phthalate	0.317	7.00	0.49	8.87
Diethyl phthalate	0.281	7.49	0.36	7.99
Dipropyl phthalate	0.220	6.50	0.23	6.65
Dibutyl phthalate	0.180	7.99	0.38	6.95
Phenols				
Phenol	0.283	3.00	0.30	4.51
o-Cresol	0.294	1.75	0.53	9.52
m-Cresol	0.542	6.50	0.44	6.39
p-Cresol	0.321	6.00	0.39	8.04
2,4-Dimethyl phenol	0.303	6.99	0.32	5.21
Catechol	0.495	5.40	0.29	8.19
Resorcinol	0.392	5.87	0.28	5.32
ketones				
Acetone	0.217	1.00	0.55	5.62
2-Butanone	0.239	9.99	0.45	3.96
4-Nonyl-2-pentanone	0.240	7.47	0.43	4.55
Isophorone	0.102	10.00	0.54	12.28

TABLE 2. RESULTS ILLUSTRATING EFFECT OF SUBSTRATE CONCENTRATION

Compound	Conc. mg/L	lag days	μ_m hr ⁻¹	r mg/mg	K_s mg/L	r mg/mg	q	Q
Benzene	20	3.0	0.135	0.32	6.17	0.17	5.19	0.52
	40	3.5	0.284	0.30	6.17			0.8412
	60	3.5	0.277	0.28	4.75			
	80	3.7	0.261	0.29	5.99			
	100	3.5	0.282	0.27	6.87			
Toluene	20	1.8	0.494	0.37	7.62	0.71	5.19	0.38
	40	2.0	0.490	0.33	7.29			0.8412
	60	2.2	0.615	0.40	7.34			
	80	2.0	0.667	0.33	8.11			
	100	2.2	0.522	0.36	7.75			
Ethyl benzene	20	2.3	0.280	0.34	9.99	0.92	5.19	0.42
	40	2.7	0.240	0.34	9.89			0.8412
	60	3.0	0.220	0.30	9.95			
	80	3.0	0.250	0.29	10.12			
	100	3.0	0.218	0.34	10.07			
Phenol	20	0.5	0.199	0.44	7.49	1.24	5.19	0.81
	40	0.5	0.264	0.44	8.00			0.8412
	60	0.5	0.281	0.40	8.89			
	80	0.8	0.317	0.38	8.41			
	100	1.0	0.283	0.39	6.16			
2,4-Dimethyl phenol	40	2.2	0.180	0.31	9.99	5.15	9.55	0.81
	80	2.0	0.258	0.28	9.99			0.9649
	100	2.4	0.303	0.32	8.92			
Resorcinol	40	1.3	0.540	0.36	3.32	2.29	6.59	0.41
	60	1.3	0.597	0.37	4.37			0.9065
	80	1.3	0.580	0.36	3.00			
	100	1.3	0.392	0.32	4.81			
Diethyl phthalate	40	2.5	0.400	0.51	7.75	1.62	6.59	0.40
	60	2.5	0.282	0.49	8.00			0.9065
	80	2.5	0.181	0.44	8.90			
	100	2.5	0.317	0.49	7.00			
Diethyl phthalate	20	2.0	0.135	0.38	8.87	2.93	5.19	0.63
	40	2.0	0.175	0.43	9.37			0.8412
	60	2.0	0.162	0.42	8.89			
	80	2.0	0.297	0.45	7.59			
	100	2.0	0.282	0.39	7.58			
Dibutyl phthalate	20	2.0	0.094	0.51	7.77	3.50	5.19	0.58
	40	2.0	0.161	0.50	7.41			0.8412
	60	2.0	0.120	0.46	9.01			
	80	2.0	0.201	0.47	7.59			
	100	2.0	0.180	0.49	7.89			

TABLE 3. RESULTS OF EFFECT OF BIOMASS CONCENTRATION

Compound	Parameter	Biomass Conc. (mg/L)	r	K	q	Q
Benzene	μ_m	20	0.220	0.282	0.201	
	r	30	0.30	0.27	0.31	
	K_s	40	6.19	4.57	7.29	
	lag	40	3.5	3.0		
						5.15 9.55 0.67 0.9649
Toluene	μ_m	0.401	0.522	0.442		
	r	0.32	0.38	0.31		
	K_s	7.85	7.75	8.98		
	lag	2.75	2.20	1.85		
					0.79	0.87
Ethyl benzene	μ_m	0.160	0.218	0.189		
	r	0.34	0.34	0.32		
	K_s	10.15	10.07	9.84		
	lag	4.8	3.0	2.8		
					0.14	0.66
Phenol	μ_m	0.299	0.283	0.159		
	r	0.37	0.30	0.34		
	K_s	3.50	3.00	4.37		
	lag	1.2	1.0	0.8		
					2.53	0.91
2,4-Dimethyl phenol	μ_m	0.332	0.303	0.238		
	r	0.38	0.32	0.34		
	K_s	6.00	7.00	6.00		
	lag	2.3	2.2	2.0		
					2.57	0.43
Resorcinol	μ_m	0.346	0.395	0.339		
	r	0.33	0.27	0.31		
	K_s	4.40	5.88	4.89		
	lag	1.5	1.3	1.0		
					0.21	0.84
Diethyl phthalate	μ_m	0.218	0.317	0.207		
	r	0.44	0.49	0.49		
	K_s	7.00	7.00	7.37		
	lag	3.1	2.5	2.7		
					1.17	0.93
Diethyl phthalate	μ_m	0.303	0.282	0.141		
	r	0.39	0.36	0.40		
	K_s	6.99	7.49	6.40		
	lag	2.1	2.0	2.0		
					6.95	0.56
Dibutyl phthalate	μ_m	0.239	0.180	0.219		
	r	0.30	0.37	0.36		
	K_s	8.22	7.80	7.80		
	lag	2.2	2.0	2.0		
					1.87	0.89

TABLE 4. RESULTS OF EFFECT OF TEMPERATURE

Compound	Parameter	Temperature (°C)	r	K	q	Q
Benzene	μ_m	15	0.163	0.282	0.292	
	r	25	0.22	0.27	0.29	
	K_s	35	7.44	6.57	7.44	
	lag		8.5	3.5	2.5	
						0.14 0.94
Toluene	μ_m	15	0.514	0.523	0.530	
	r	25	0.32	0.38	0.35	
	K_s	35	7.07	7.75	6.27	
	lag		6.5	2.2	2.0	
						0.83 0.28
Ethyl benzene	μ_m	15	0.210	0.216	0.221	
	r	25	0.32	0.34	0.36	
	K_s	35	10.51	10.07	9.15	
	lag		6.5	3.0	2.3	
						0.46 0.44
Phenol	μ_m	15	0.220	0.283	0.332	
	r	25	0.28	0.30	0.34	
	K_s	35	3.50	3.00	4.87	
	lag		2.5	1.0	0.8	
						27.74 26.38
2,4-Dimethyl phenol	μ_m	15	0.267	0.303	0.330	
	r	25	0.28	0.32	0.27	
	K_s	35	7.01	7.00	5.50	
	lag		8.5	2.2	1.0	
						7.21 18.83
Resorcinol	μ_m	15	0.360	0.395	0.420	
	r	25	0.22	0.28	0.29	
	K_s	35	5.00	5.87	5.50	
	lag		2.5	1.2	1.0	
						3.98 13.73
Diethyl phthalate	μ_m	15	0.198	0.317	0.331	
	r	25	0.43	0.49	0.41	
	K_s	35	6.00	7.00	6.89	
	lag		5.50	2.50	2.00	
						1.43 0.89
Diethyl phthalate	μ_m	15	0.225	0.282	0.334	
	r	25	0.30	0.36	0.35	
	K_s	35	8.98	7.49	7.37	
	lag		5.50	2.00	1.50	
						20.72 23.54
Dibutyl phthalate	μ_m	15	0.172	0.180	0.188	
	r	25	0.29	0.37	0.38	
	K_s	35	9.84	7.80	9.27	
	lag		6.8	2.0	1.5	
						0.94 0.75

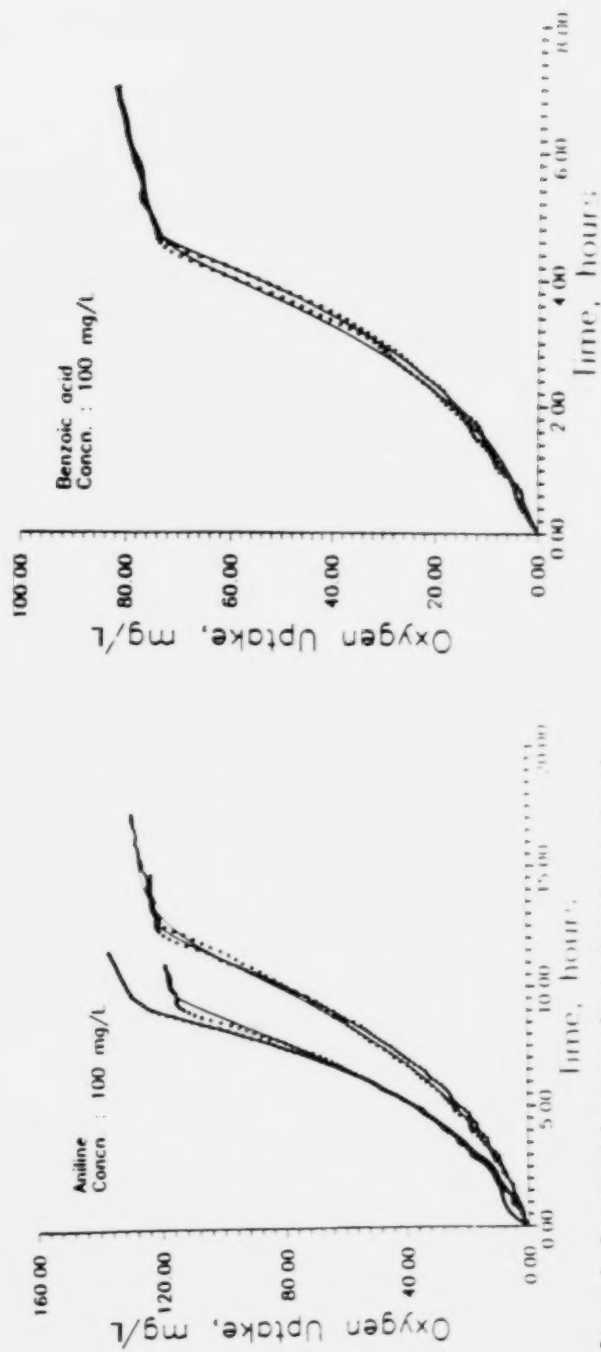


Figure 1. Oxygen uptake curves for biodegradation of aniline.

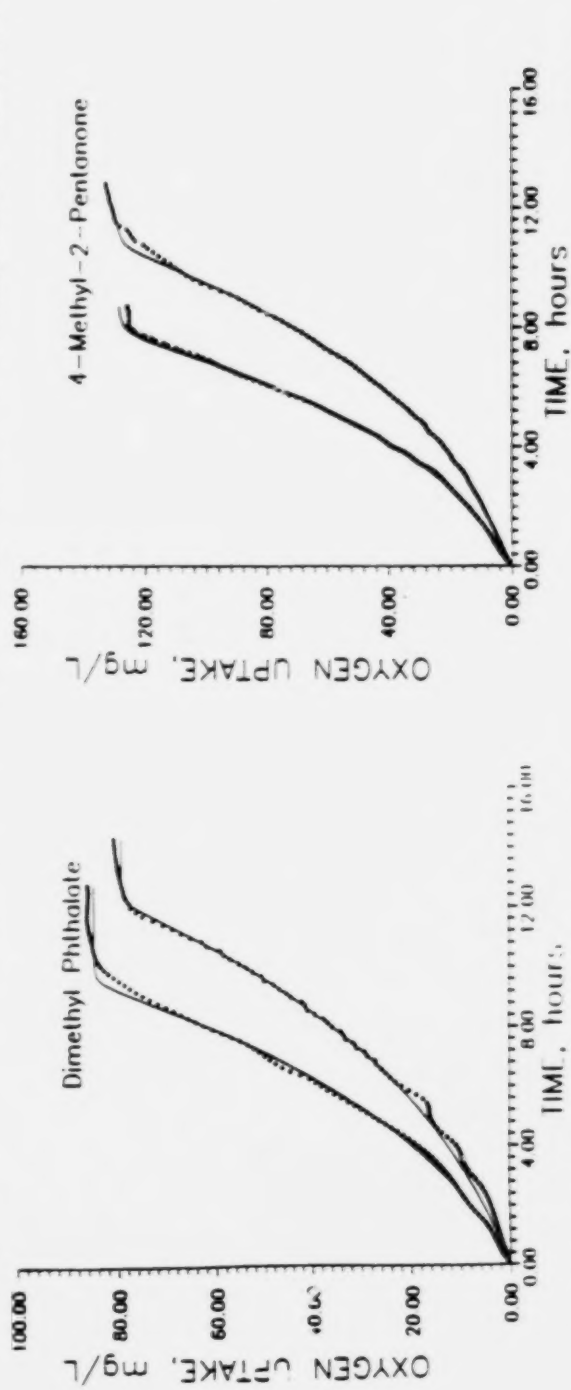


Figure 3. Oxygen uptake curves for dimethyl phthalate at 100 mg/L.

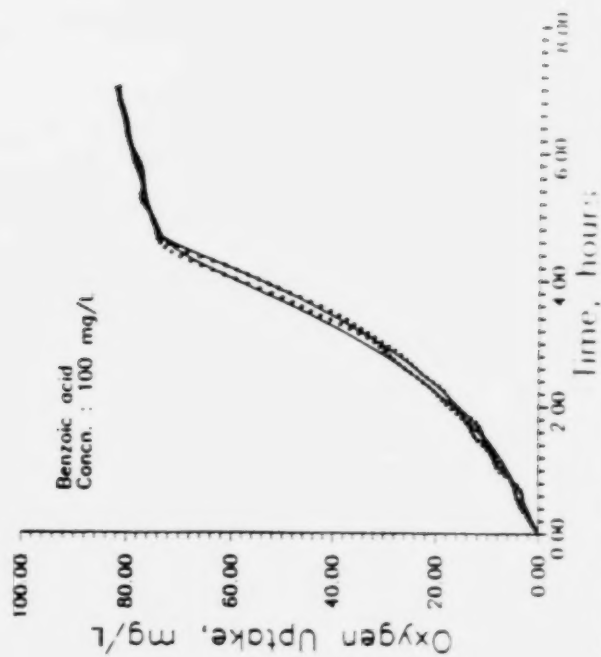


Figure 2. Oxygen uptake curves for biodegradation of benzoic acid.

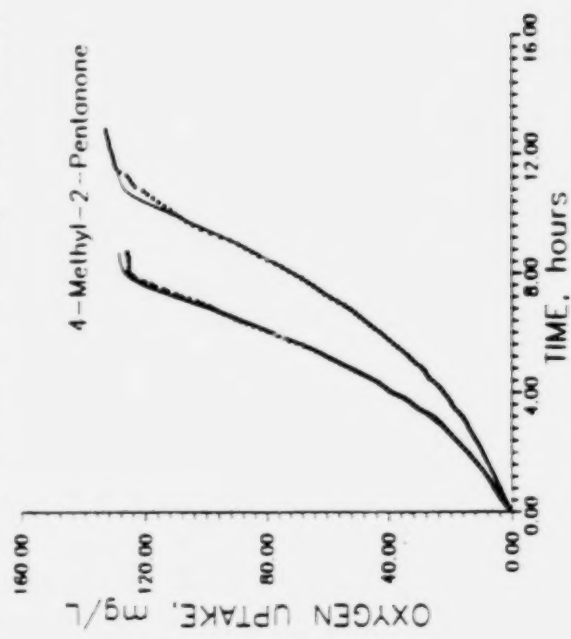


Figure 4. Oxygen uptake curves for 4-methyl-2-pentanone at 100 mg/L.

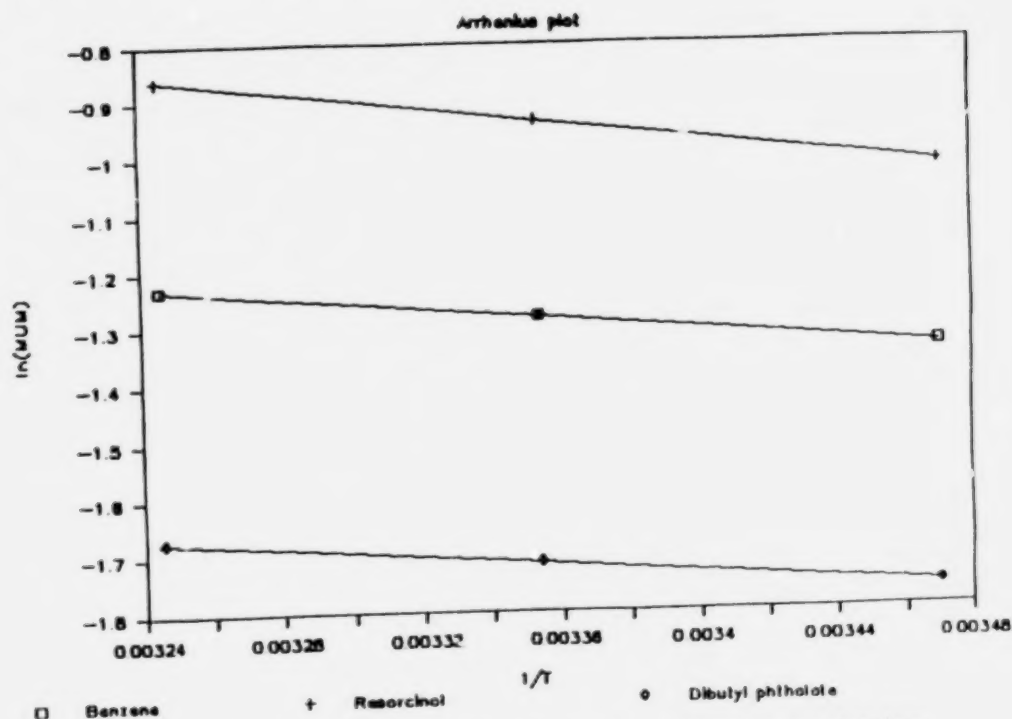


Figure 5. Arrhenius plot for benzene, resorcinol and dibutyl phthalate.

TABLE 5. RESULTS OF EFFECT OF SLUDGE SOURCE

Compound	Parameter	Little Miami	T. & E.	Monsanto	BP
Benzene	k_0	0.282	0.116	0.122	0.672
	r	0.27	0.29	0.22	0.22
	K_1	6.57	8.77	7.64	9.24
	K_1 extant	54.0	53.0	56.5	52.0
Toluene	k_0	0.523	0.376	0.141	0.776
	r	0.36	0.32	0.26	0.29
	K_1	7.75	6.52	4.51	8.13
	K_1 extant	67.5	62.0	60.5	64.0
Ethyl Benzene	k_0	0.214	0.130	0.240	0.499
	r	0.34	0.30	0.26	0.25
	K_1	10.07	2.90	7.97	10.12
	K_1 extant	93.0	95.5	99.0	99.0
Phenol	k_0	0.283	0.154	0.183	0.316
	r	0.30	0.39	0.39	0.22
	K_1	3.00	9.50	5.00	8.99
	K_1 extant	95.0	95.0	94.0	97.0
2,4-Dimethyl phenol	k_0	0.303	0.179	0.158	0.113
	r	0.32	0.34	0.30	0.21
	K_1	7.00	3.00	8.50	7.00
	K_1 extant	90.0	95.0	87.0	88.0
Resorcinol	k_0	0.396	0.159	0.351	0.394
	r	0.28	0.39	0.31	0.30
	K_1	5.87	4.88	8.77	6.50
	K_1 extant	87.5	95.5	90.0	92.0
Dimethyl phthalate	k_0	0.317	0.152	0.118	0.460
	r	0.49	0.41	0.40	0.47
	K_1	7.00	2.00	5.25	5.00
	K_1 extant	99.0	99.0	99.9	99.5
Diethyl phthalate	k_0	0.282	0.140	0.114	0.413
	r	0.36	0.47	0.32	0.32
	K_1	7.50	2.00	10.00	7.48
	K_1 extant	88.5	90.0	88.0	84.5
Dibutyl phthalate	k_0	0.180	0.219	0.265	0.487
	r	0.37	0.61	0.48	0.54
	K_1	7.89	7.28	6.12	5.23
	K_1 extant	88.5	84.5	88.0	88.5

CHEMICAL COMPATIBILITY OF
GEOTEXTILES, GEONETS AND PIPES WITH HAZARDOUS WASTE

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ABSTRACT

Despite the advanced technology displayed by the United States chemical industry, there exists little comparable technological capacity to deal with the billions of tons of improperly disposed toxic chemical waste. Due to this lack of technology, research in the field of geosynthetics used in hazardous waste containment began approximately ten years ago. One problem facing the advancement of modern geosynthetic technology is the lack of consistent testing methods. For this purpose, a project was undertaken to develop a technological base for predicting the long-term durability and compatibility of geotextiles, geonets and pipes in contact with hazardous waste.

In the initial phase of this project, an extensive literature search was conducted on existing information to investigate the performance and failure criteria for these geosynthetics. From this literature review, an article has been prepared on geotextiles, geonets, and pipes used in landfill sites, types of polymeric materials, exposure and characterization methods. In addition to focusing on the available information of the chemical compatibility of geosynthetics, this review has identified some areas of current and future study, such as the use of analytical techniques to determine the molecular interaction between geosynthetic materials and leachate components.

The second phase, currently in the planning stage, will address some of the significant questions and problems of chemical compatibility testing of geosynthetics. Some of these concerns are the determination of test methods that will reflect field performance and development of novel accelerated-aging techniques. Handling of chemicals and the equipment required for the establishment of safety procedures is another concern. A more complete understanding of the failure mechanisms will allow for better design and material choices in future landfill sites. New guidelines have been recommended for the evaluation of geotextiles, geonets and pipes used in hazardous waste facilities. These recommendations are based upon the information obtained in the first phase of this study and will be the subject of the experimental work in phase two.

This paper has been reviewed in accordance with the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

INTRODUCTION

The need to develop a technological base for predicting the long-term durability and compatibility of geotextiles, geonets and pipes with hazardous waste has been evident for some time. A cooperative study consisting of two phases was initiated to determine the inadequacies of present practices among engineers in this industry. The first of two phases included a comprehensive survey which enabled those involved to define the technology base presently available to evaluate the chemical compatibility of these geosynthetic materials. The following general objectives were proposed:

- * Providing an up-to-date review of data produced within the government, industry and academia to assess the chemical compatibility of geosynthetic products other than geomembranes used in construction of hazardous waste landfills;
- * Recommendation of improved test methods to assess chemical compatibility of geotextiles, geonets and pipes;
- * Recommendation of criteria for evaluation of chemical compatibility data for material selection and permit application review purposes.

In addition to the proposed objectives, the final recommended test methods and evaluation criteria should include:

- * Measurement of physical or molecular-level characteristics that can reflect the product's ability to perform its design function;
- * Minimization of testing laboratory cost and elimination of tests which do not reflect field performance or are redundant; and
- * Production of meaningful results within a reasonable testing time.

PHASE I

The initial phase consisted of an extensive information gathering process that included compilation of a database and subsequent preparation of a review article, assembly of data from mail surveys, phone and personal interviews with manufacturing organizations, testing laboratories and facility designers. This information gathering allowed for the establishment of performance and failure criteria, review of analysis and existing data in order to define the Phase II test plan. Specifically this portion of the project provided:

- * A table of chemical resistance recommendations for geosynthetics;
- * A survey of methods currently used by environmental engineering firms and commercial testing labs to assess chemical compatibility;

- * The suggestion of a generalized procedure that would incorporate current testing protocols utilized by labs now performing chemical compatibility testing; and
- * An experimental plan for Phase II to further define laboratory procedures and evaluation criteria.

Overall, as a result of this work, polymer degradation phenomena will be further understood which will establish new modes of technology exchange among academia, industry and the government regulatory community.

TEST METHODS

With the exception of the EPA's method 9090, no standardized methods exist for analyzing the durability of geosynthetic materials before or after exposure to the environment or aggressive chemicals. In the past, the durabilities of the geosynthetics have traditionally been assessed on the basis of mechanical property test results. The evaluation of microstructural or molecular changes which can cause changes in bulk properties has been performed, but not extensively. Analytical techniques developed for the evaluation of polymer properties can aid in the determination of changes in the molecular structures of the base polymers used to manufacture the geosynthetic(1).

Specialized Analytical Techniques

Analytical techniques have found limited use in this field so far, but hold great promise for the future. These specialized techniques elucidate the relationship between microstructural changes in the base polymer and physical and mechanical property changes of geosynthetics. The information obtained will provide a more complete understanding of the interaction between geosynthetic materials and the leachates they contain. From this a more accurate prediction of the service life-time of geosynthetics can be deduced. These techniques, described below, include analytical methods commonly used to characterize components on the molecular level.

Thermal Analysis -- Thermal analysis includes a range of techniques for determining the temperature dependence of the polymer property changes. Mass, heat capacity, heat of chemical or physical change, mechanical response and volume are the most commonly observed physical property changes examined by thermal analytical methods. A good indicator of structure-behavior relationships in polymer applications, this measurement of property changes versus temperature has prompted the development of these techniques specially for polymer work(2).

Spectroscopy -- Spectroscopic techniques provide information on the compositional and structural characteristics of a polymeric material. Infrared (IR) spectroscopy is particularly useful in the identification of characteristic functional groups and molecular configurations by simple inspection and reference comparison. The sample is subjected to infrared radiation of successively decreasing frequencies. A series of spectral bands is generated, each of which correlates to a particular frequency or range of frequencies where the organic (functional groups in the plastic) material absorbs radiation. These characteristic

absorption frequencies indicate certain functional groups in the polymer(1). Comparative IR techniques can be a sensitive method to detect changes in the polymer.

Chromatography -- Chromatographic methods allow the separation, isolation and identification of closely related components in complex mixtures. Due to the diversity of these separation techniques, other analytical methods do not possess the ability to identify components from mixtures with such accuracy. Chromatography identifies components in the gaseous, liquid or solid state, which may include substances that have been absorbed into the geosynthetic material itself. This valuable information can be used to identify various components of leachates or products that result from polymer degradation.

Microscopic Analysis -- The use of magnification to evaluate geosynthetic materials is provided by various types of microscopic techniques. Microscopy supplies rapid, direct observational information about the surface as well as the internal microstructure and defect distribution within the materials. Microscopic analysis is also a valuable tool for the examination of geosynthetic materials before and after exposure to aggressive chemical media.

Viscosity Measurements -- Relative changes in molecular weight may be monitored by melt flow index (MFI) testing and dilute solution viscosity (DSV) testing. Both of these tests measure either the melt or solution viscosity of the polymer used in the geosynthetic product. These measurements are related to the average molecular weight of the polymer which in turn is related to the properties of the polymer.

CURRENT PRACTICE

According to RCRA Part B permit applications on file at several EPA regional offices, until very recently, the general practice has been to cite either manufacturers' recommendations or general chemical resistance data from technical references, such as plastics' applications' handbooks, to demonstrate the compatibility of the geosynthetics other than liners, proposed with a specific waste of known composition. These referenced data or recommendations were submitted along with Method 9090(3) results for the proposed geomembrane liners in the original Part B application.

More recently the trend has been to perform laboratory testing for all geosynthetics to be used in the proposed containment facility design. This testing may be "piggybacked" with the chemical compatibility testing required for geomembranes as required by Method 9090. Several commercial laboratories have performed a significant number of chemical compatibility studies in which geotextiles, geonet, pipe or a combination of these were tested against a specific waste leachate in a manner analogous to Method 9090 as applied to liners.

Product Sampling Procedures

Variability in properties among samples of geosynthetics must be understood, since chemical compatibility testing depends on the ability to compare properties measured before and after chemical immersion exposure.

Geotextiles, in particular, demonstrate significant variability within a given roll or

product lot in weight, thickness and mechanical properties. This is a normal characteristic and relates to the manufacturing methods used. This variability in properties must be understood, since chemical compatibility testing depends on the ability to compare properties measured before and after chemical immersion exposure. Interpretation problems could result if, for example, a much thicker section of geotextile were cut into samples and tested at zero days, while samples tested at a later immersion interval were cut from a thin area.

This problem has been recognized by the commercial laboratories, and four ways of eliminating or controlling variability are in use. These methods have been developed so that changes observed before and after exposure may be attributed to the degradation rather than variations within the material.

The first method involves recording the weight and thickness of each specimen to be included in the immersion testing. Each specimen is assigned a coded identification number and individual specimen weights and thickness are recorded into a database which will be kept for reference throughout the project. A numbered tag is attached to each specimen. Specimens are not screened; each weighed specimen is included in the test matrix regardless of weight or thickness. Prior to assigning specimens to exposure baths or intervals, all cut, weighed and tagged samples are "shuffled" physically so that weights and thicknesses throughout the range are evenly distributed. When test data are reported, original weights and thickness from the unexposed specimen database are included with the test results. Widely varying data may be identified and considered in the context of any apparent trends in the data. This method is often preferred, but is not used exclusively.

The second method involves a pre-screening of cut specimens. First, average roll values for weight and thickness are developed by measuring and weighing 20 specimens cut randomly from various parts of the roll. Then, specimens for each physical property to be measured at each exposure interval are cut from the original roll. The quantity to be cut for each property is increased over that needed for the actual testing by a factor of 1.5 or more. After cutting, each individual specimen is weighed. If the weight falls outside one standard deviation from the established roll values, that specimen is rejected and discarded. Only specimens falling within one standard deviation for both weight and thickness are tested. Pre-screened specimens are not marked or identified, and weights are not recorded.

The third method involves cutting all specimens required for baseline and immersion interval testing from one selected region across the width and along the length of the supply roll of geotextile. Weight and thickness compliance with minimum roll value specifications is verified before testing begins. This method recognizes that due to the manufacturing procedures used, product weight and thickness tend to vary in a consistent way across any given roll.

The fourth method consists of testing seven replicates for each mechanical property test, and rejecting the two of the seven which produce data outside a reasonable standard deviation so that the reported test value is an average of five replicates. No pre-screening or sample selection is done prior to testing.

Of the six testing laboratories contacted, five reported having significant experience with evaluating chemical compatibility of geotextiles. Of these five, one uses the first method, two the second, one the third and one the fourth for addressing the problem of geotextile variability. Rationale for the first method is that an assessment of product variability can be obtained as a "by-product" of chemical compatibility testing, since weights and thicknesses are recorded and reported. Also, the recorded physical data may prove useful in the later data evaluation, for example, to explain data which show inconsistencies or unexpected trends. Rationale for the second, third and fourth methods is that chemical compatibility testing is intended to determine whether a specific leachate interacts with a geosynthetic product in any measurable way; since this issue is unrelated to product variability, the best approach is to eliminate this variability as much as possible, thereby simplifying data analysis.

The sampling problems described are less critical for geonet and pipe products. For these, special procedures analogous to those described above have not been developed. Product sampling procedures are based on requirements of the various test method standards.

Immersion and Leachate Handling Procedures

Immersion bath design, leachate preparation procedures and leachate handling for geonet, geotextile and pipe compatibility tests are commonly performed following Method 9090 guidelines. It has been found that these general procedures, originally developed for geomembranes, are equally suited for the other products, and by using the same procedures and equipment a consistent test exposure protocol may be applied to all materials included in the test plan. Equipment differs in design and construction details; however, each commercial laboratory includes the basic elements as required by Method 9090 to maintain leachate immersion baths at two temperatures, while providing for uniform dispersion within the tank or vessel, exposure of all specimen surfaces, and containment of evaporating volatiles.

Test Method Selection Criteria and Test Method Modifications

Since standardization has been lacking for chemical compatibility testing of geotextiles, geonet and pipe, the selection of test methods for evaluation of property changes caused by leachate exposure has been left up to the individual facility owner or designer. From an engineering standpoint it is desirable to learn whether design or functional performance properties of the geosynthetic component are affected by extended leachate exposure. However, it has not been practical in most cases to measure performance properties, and it has become standard practice to select index tests for inclusion in chemical compatibility test programs. The goal in selecting and evaluating results of index tests is to determine whether the leachate is interacting with the geosynthetic product in a way that might degrade the material or its ability to perform an intended design function over the long term. Though index test results are not directly transferable to field performance, they provide a scale by which degradation can be monitored.

Criteria used to select index or performance tests for inclusion in chemical

compatibility studies can be summarized as follows:

- * The test must provide reproducible results and be relatively independent of experimental factors or operator-introduced errors.
- * The test must require relatively small individual specimens so that leachate volume can be minimized, and to allow a sufficiently large number of replicates (especially critical for geotextiles).
- * The test should not measure a property or simulate an exposure that would be completely uncharacteristic of the proposed design function.

Chemical compatibility testing as outlined in Method 9090 has been applied to the evaluation of geotextiles, geonet and pipe in practice. The introduction of a standard chemical compatibility test method expanded to include these geosynthetic products will be welcomed by participants in the commercial geosynthetic testing market, as well as by designers and users of the geosynthetics.

Each laboratory surveyed reported that, in practice, standard index and performance test methods are modified to meet the special problems associated with chemical compatibility testing. A summary of test method modifications reported is given below for each class of geosynthetic in this study.

As noted in the previous section, varying numbers of replicates are tested for determination of index properties. For geotextiles, two of five laboratories test five samples; one tests seven, then rejecting two which generate data outside a reasonable standard deviation, and two test ten replicates per determination. One laboratory recommends evaluating permittivity of geotextiles using common samples, i.e. samples that are not discarded after testing, but re-immersed and retested at each succeeding interval.

For chemical compatibility testing there is general agreement to test in only one direction (usually the machine direction) for those index methods which are direction-oriented. One laboratory recommends use of a modified grab test substituting a 2-inch-wide specimen for the standard 4-inch grab sample.

Monitoring weight change as a function of exposure, as required for liners in Method 9090, is difficult for geotextiles since it would require that each geotextile specimen be fully dried prior to weighing and subsequent destructive testing. Some labs have attempted to get around this problem by including specimens specifically assigned for weight and dimensional determinations which are not destructively tested. However, problems associated with drying of geotextiles have been difficult to resolve due to the physical nature of the products.

Four of six labs responding reported using a non-standard strip tensile test for evaluating geonets during chemical compatibility studies. Strip width varies from two to three inches; two laboratories test across three parallel strands. One laboratory applies the tensile grab test standard, ASTM D 1682(4), for geotextiles to geonet. In general, only

one of the two possible directions is tested. The strip tensile test is preferred to standard methods such as wide width tensile strength because of sample size. One laboratory uses a quality control specification developed by a geonet manufacturer for strip tensile testing of net in one direction. No ASTM standard exists for narrow strip tensile testing of geonet.

One lab applies the ASTM D 751(5) ball burst method (using a 1-inch ball) for evaluation of geonet in chemical compatibility studies. One laboratory uses a special hydraulic transmissivity test device which accepts 4-inch square geonet specimens (a more generally accepted dimension for hydraulic transmissivity determinations is 12-inch square, although the 4-inch size is compliant with the ASTM D 4617⁽⁶⁾, the standard for transmissivity).

The most common test applied to pipe in waste containment applications is pipe stiffness: ASTM D 2412(7). However, the standard test requires long and unwieldy section of pipe. The laboratories surveyed have used 3- to 5-inch long cut sections of pipe for chemical compatibility testing. Even with shorter specimens, pipe specimens are bulky and require large volumes of leachate for immersion; the number of replicates which can be immersed is limited to two to four, depending on pipe dimensions and internal procedures.

Two laboratories have reported using tensile bars cut from walls of solid pipe for determining tensile strength as a function of exposure according to ASTM D 638(8) or a similar method. This approach is not suitable for corrugated or slotted pipe because of the uneven wall profile.

This section has provided an overview of how chemical compatibility testing as outlined in Method 9090 has been applied to the evaluation of geotextiles, geonet and pipe in practice. It can be seen that many widely varying adaptations are currently in use. The introduction of a standard chemical compatibility test method expanded to include these geosynthetic products will be welcomed by participants in the commercial geosynthetic testing market, as well as by designers and users of the geosynthetics.

EVALUATION AND INTERPRETATION OF CHEMICAL COMPATIBILITY TEST DATA

Current practices used within the geosynthetics industry to determine chemical compatibility of geosynthetics reveal inconsistencies and inadequacies for testing geotextiles, geonets and pipes. The problem facing the design and regulatory community is to find a way to assess the data produced from these testing programs. Evaluation of useful lifetime through accelerated aging tests (accelerated life testing-ALT) has been sorely neglected due to the complexity of data interpretation and the lack of understanding of these tests as applied to geosynthetic chemical compatibility. The interaction of geosynthetic polymer and fibers with chemical wastes may result in a change in physical properties of the geosynthetics, either from chemical attack or from a solvation process caused by mutual solubility of the waste material with the geosynthetic. However, the designer need only be concerned if the design function of the geosynthetic can no longer be fulfilled after exposure to the waste or leachate.

Earlier in this paper, it can be seen that widely varying opinions were received.

This is a complex issue, and there is probably some merit to each of the arguments presented. The SWTSU survey team concluded that to interpret the significance of data does in fact require an informed analysis of the compatibility results in light of considerations specific to the site, facility design, and synthetic and natural materials proposed. The compatibility results themselves should be considered together as a whole and a decision to accept or reject the material on one physical test value at one isolated time interval or temperature should be avoided. That is to say, observed degradation should be consistent across several measured properties or test values if it is to be considered significant. Statistical analysis of tabulated compatibility data may be appropriate in many cases.

RECOMMENDATIONS

The specific methods used to evaluate these geosynthetic products vary between the various laboratories. Standards for chemical compatibility testing of geosynthetic products should be within the framework of consensus standards organizations such as ASTM (particularly Committee D-35), and that regulators cite these industry standards when they become available. Also, analytical techniques such as thermal analysis and spectroscopic methods should be performed before and after a chemical compatibility test. There are two reasons for doing this: (1) to provide additional data to assess any effect of leachate immersion on the base polymer, and (2) to provide a fingerprint for future assurance that the correct material was installed.

Testing should provide valuable data not within the scope of existing standard test methods. Also, using appropriate modifications to existing test methods and non-standard methods greatly reduces the volume of leachate required for chemical compatibility testing, thus reducing the cost burden imposed on the facility designer. In addition, industry should develop standard methods designed to meet the needs for index tests which provide full physical characterization of these geosynthetics using small samples. The evaluation of chemical compatibility data is an involved process that requires consideration of details specific to the site, facility design, waste components and the materials tested.

PHASE II

The second phase of this research involves investigating and recommending a testing protocol for geosynthetic chemical compatibility testing. Although this investigation is only in the planning stage, the section below gives a summary of the questions and concerns being addressed by this plan.

These questions and concerns have been grouped into three categories. The first category is that of field performance versus laboratory or index tests. There are two major concerns here. One, what amount of failure in an index test constitutes a field failure and two, which index test is the most effective for each type of geosynthetic material. The next category involves accelerated aging. Test conditions must be developed so that aging or degradation can be observed in a short period of time. Subsequently, some means of extrapolation must be applied to provide a prediction of the service life-time of the geosynthetic under normal conditions. The last category is to establish a correlation

between data obtained about the molecular interactions and the properties of the bulk material. Such a correlation would help in several areas including QA/QC, early detection of degradation and provide a more complete understanding of degradation process.

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STABILIZATION/SOLIDIFICATION FOR
TREATMENT OF SUPERFUND SOILS

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ABSTRACT

The overall objective of this research was to determine the effectiveness of the stabilization/solidification process in reducing the mobility (as measured by the Toxicity Characteristic Leaching Procedure) of metals, pesticides, and polychlorinated dibenzofurans in actual Superfund soils. Another objective of the study was to determine how well the stabilization/solidification process performed on actual Superfund soil versus a synthetic soil matrix.

Superfund soils from the Tri-State Metals Plating site in Columbus, Indiana, and the Syncon Resins Site in Kearney, New Jersey, were selected for bench-scale stabilization/solidification testing at the International Technology Corporation (IT) Technology Development Laboratory in Knoxville, Tennessee. Screening tests were conducted to determine optimum water ratios and binder ratios with three commonly used binders--portland cement, lime/fly ash, and kiln dust. Water-to-total-solids ratios of 0.30 to 0.45 and binder-

to-soil ratios of 0.5, 0.75, and 1.0 were used for testing. Samples prepared in triplicate were allowed to cure under controlled conditions for 28 days and then subjected to unconfined compressive strength (UCS) testing. The minimum binder-to-waste ratio for each binder type that exhibited a UCS value greater than 50 psi was selected for chemical analysis. The chemical analyses were performed by IT Corporation and a contract laboratory program (CLP) laboratory (Ecology and Environment, Inc. in Buffalo, New York).

Analytical results are presented for the untreated and stabilized/solidified Tri-State Metals Plating and Syncon Resins soil, volatile organic compound (VOC) headspace analyses during sample curing, and the portland cement, kiln dust, and lime/fly ash binders. Both untreated and treated Tri-State soils were subjected to total waste analysis (TWA) and toxicity characteristic leaching procedure (TCLP) metals; total organic carbon (TOC); humic acid content; grain size distribution; and cation exchange capacity. Both treated and untreated Syncon Resins soils were analyzed for TWA and TCLP metals, pesticides, and polychlorinated dibenzofurans; TOC; humic acid content; grain size distribution; and cation exchange capacity. Binders were analyzed for TWA and TCLP metals. Also reported are UCS values, bulk densities, and curing conditions.

This paper also includes a comparison of results from tests conducted during Phase I, which involved stabilization/solidification of a synthetic soil matrix, with results from testing conducted on actual Superfund site soils (Phase II). Differences in experimental procedures (e.g., blending, curing, VOC headspace sampling), analytical methodology, and physical/chemical results are discussed.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer review and administrative review policies and approved for presentation and publication.

INTRODUCTION

Section 3004 of the Resource Conservation and Recovery Act (RCRA) of 1976, as amended by the Hazardous and Solid Waste Amendments (HSWA), mandates a ban on the land disposal of hazardous wastes unless they have been treated to prevent the migration of hazardous constituents into the environment. The U.S. Environmental Protection Agency (EPA) must set land disposal restriction (LDR) treatment standards, based on best demonstrated available technology (BDAT) and performance levels, that substantially diminish waste toxicity or greatly reduce the likelihood of constituent migration so as to minimize short- and long-term threats to human health and the environment.

Land disposal restrictions apply to soil and debris when they are contaminated with a restricted RCRA hazardous waste. Because of the complex nature of many soil and debris matrices, meeting treatment standards for wastes mixed with soil and debris may be difficult. Therefore, EPA is undertaking a rulemaking that will set LDR treatment standards specifically for soil and debris.

BACKGROUND

Under Phase I of EPA's BDAT research program (conducted from April to November 1987), a surrogate soil containing a wide range of chemical contaminants typically occurring at Superfund sites was prepared for use in bench-scale or pilot-scale performance evaluations of five available treatment technologies: 1) physical treatment (soil washing), 2) chemical treatment using a potassium polyethylene glycol reagent (KPEG), 3) thermal desorption, 4) stabilization/solidification, and 5) incineration. Under Phase II of EPA's BDAT research program (conducted from April 1988 to March 1990), contaminated soils from several Superfund sites were used to reevaluate four of these treatment technologies at the bench scale: soil washing, KPEG, low-temperature thermal desorption, and stabilization/solidification. Incineration was not evaluated in Phase II because of the expense involved in conducting pilot-scale evaluations and the large quantity of data available on incineration of hazardous waste.

A previous EPA report (1) presented the performance evaluation results obtained during Phase II for physical treatment (soil washing), chemical treatment (KPEG), and thermal desorption, and compared results obtained during Phases I and II. This paper addresses the performance evaluation results obtained during Phase II for stabilization/ solidification. A comparison of Phase I and Phase II experimental results for stabilization/solidification is also provided.

PURPOSE AND OBJECTIVES

The purpose of the paper is twofold: 1) to present the data generated by the stabilization/solidification of Superfund soil from Syncon Resins near Kearney, New Jersey, and Tri-State Metals Plating in Columbus, Indiana, and 2) to compare the results obtained on actual Superfund soil (Phase II) to the results obtained on synthetic soil (Phase I).

EPA specified several objectives in the performance of these stabilization/solidification tests:

- 1) To calculate the percent reduction of leachable metals, pesticides, herbicides, and furans.
- 2) To determine the concentration of metals, pesticides, herbicides, and furans in the stabilized/solidified soil TCLP extracts.
- 3) To estimate VOC emissions from the stabilization/solidification process.
- 4) If possible, to draw conclusions from a comparison of Phase I and Phase II stabilization/solidification data.

EXPERIMENTAL PROCEDURES

The purpose of the Phase II program was to evaluate the effectiveness of the stabilization/solidification treatment technology on two Superfund site soils--the Tri-State Metals Plating site at Columbus, Indiana, and the Syncon Resins site at Kearney, New Jersey. Three generic binding agents (portland cement, kiln dust, and a 1:1 mixture of lime/fly ash) were used to prepare soil/binder blends, and the performance of each was evaluated with respect to unconfined compressive strength development and TCLP leaching of contaminants. No proprietary chemicals were used.

All physical and chemical analyses were performed by IT Corporation in Knoxville, Tennessee, and Ecology and Environment, Inc., in Buffalo, New York. Analytical procedures and results of Quality Assurance testing are included in the full project report (2).

DESCRIPTION OF BINDERS AND SOILS

The portland cement binder was a standard Type I cement manufactured by the Dixie Cement Co. of Knoxville, Tennessee. The kiln dust used was Pozzallime Calcic Powder distributed by Mineral By-Products, Inc. of Marietta, Georgia. The composition of the kiln dust was specified as 25 to 45 percent CaO, 15 to 30 percent CaCO₃, and lesser amounts of oxides of aluminum, iron, silicon, and magnesium. The fly ash used was IFA Stabilizer, a power plant fly ash distributed by Western Ash Co. of Phoenix, Arizona, and composed of nearly equal amounts of SiO₂ and CaO. The fly ash was added to an equal weight of reagent grade Ca(OH)₂ powder (Mallinkrodt, LOT 4195 KCHX) and mixed thoroughly.

The Syncon Resins soil consists primarily of alluvial sand, silt, clay, and detritus. Its texture is heterogeneous and spongy, and it has a nonuniform liquid holding capacity. This soil is contaminated with heavy metals, pesticides, herbicides, and furans.

The Tri-State Metals Plating soil is the product of loamy glacial outwash and calcareous sand and gravel. Its clay-like texture is interspersed with granular particulate of greatly varying sizes. This soil is contaminated with heavy metals. The physical and chemical data on these soils are presented in Tables 1, 2, and 3.

RESULTS

Tables 4 and 5 summarize the TCLP data obtained for untreated and treated Tri-State Metals Plating and Syncon Resins soils. The percent reduction was calculated for each pollutant using the following equation:

$$(1 - \frac{a}{b}) \times 100 = c$$

TABLE 1. SYNCON RESINS SOILS

Parameter	Result
Volatiles, $\mu\text{g/kg}$ *	
Methylene chloride	69 B [†]
Toluene	68 B
Semivolatiles, $\mu\text{g/kg}$ *	
Pyrene	1,600
Bis(2-ethylhexyl)phthalate	780
Pesticides/herbicides/PCBs, $\mu\text{g/kg}$	
Gamma-BHC (lindane)	1,100
4,4'-DDE	8,600
4,4'-DDT	88,000 ^{††}
2,4-D	280
Dioxins/furans, $\mu\text{g/kg}$	
TCDD	ND (0.11) [§]
PeCDD	ND (0.21)
HxCDD	ND (0.60)
TCDF	12.9
PeCDF	18.4
HxCDF	12.7
Metals, mg/kg	
Antimony	<4.49
Arsenic	581
Barium	166
Beryllium	0.57
Cadmium	1.29
Chromium	65.3
Copper	91.5
Lead	224
Mercury	0.75
Nickel	20.7
Selenium	<0.18
Silver	0.74
Thallium	<6.29
Vanadium	42.2
Zinc	167
TOC, mg/kg	57,800
CN, mg/kg	0.31
Sulfide, mg/kg	194
pH, S.U.	6.58

* Only results greater than the quantitation limit (five times the detection limit) are reported.

[†] This flag is used whenever the analyte is found in the blank as well as a sample.

^{††} Above quantitation limit, estimated value.

[§] ND = not detected at the specified detection limit (method detection limit).

TABLE 2. TRI-STATES METALS PLATING SOIL

Parameter	Result
Volatiles, $\mu\text{g/kg}$ *	
Methylene chloride	14 B [†]
Toluene	27
Semivolatiles, $\mu\text{g/kg}$	ND ^{††}
Pesticides/herbicides/PCBs ($\mu\text{g/kg}$)	
Aroclor-1016	550
Dioxins/furans, $\mu\text{g/kg}$	
TCDD	ND (0.19)
PeCDD	ND (0.13)
HxCDD	ND (0.16)
TCDF	ND (0.12)
PeCDF	ND (0.12)
HxCDF	ND (0.17)
Metals, mg/kg	
Antimony	<3.01
Arsenic	8.12
Barium	44.4
Beryllium	<0.21
Cadmium	49.9
Chromium	506
Copper	99.2
Lead	267
Mercury	<0.12
Nickel	159
Selenium	<0.17
Silver	<0.37
Thallium	<6.07
Vanadium	12.8
Zinc	79.0
TOC, mg/kg	9430
CN, mg/kg	67.8
Sulfide, mg/kg	72
pH, S.U.	7.20

* Only results greater than the quantitation limit (five times the detection limit) are reported.

[†] This flag is used whenever the analyte is found in the blank as well as a sample.

^{††} ND = not detected at specified detection limit (method detection limit).

TABLE 3. GRAIN SIZE DISTRIBUTION OF CANDIDATE TEST SOILS
(wt. percent)

Site soil	Coarse sand (>0.5 mm)	Fine sand ($0.05-0.5$ mm)	Silt ($0.002-0.05$ mm)	Clay (<0.002 mm)
Syncon Resins [*]	47.8 29.8	29.1 47.0	15.1 15.0	8.0 8.2
Tri-State Metals [†]	27.3 26.0	36.3 36.2	24.9 26.6	11.5 11.2

^{*} The soil is primarily alluvial sand, silt, clays, and detritus (landfill soil).

[†] The soils at this site are developed over loamy glacial outwash and calcareous sand and gravel.

TABLE 4. CONCENTRATIONS OF METALS IN TCLP LEACHATES OF TREATED AND UNTREATED ALIQUOTS OF TRI-STATE METALS SOIL AND CORRESPONDING PERCENT REDUCTION VALUES

Analyte	Untreated soil		Treated soil					
			Portland cement		Lime/fly ash		Kiln dust	
	Conc., mg/L	Conc., mg/L	Conc., mg/L	% reduction	Conc., mg/L	% reduction	Conc., mg/L	% reduction
Antimony	<0.060	<0.060	<0.060	NA [†]	<0.060	NA	<0.060	NA
Arsenic	<0.005	<0.005	<0.005	NA	<0.005	NA	<0.005	NA
Barium	1.016	0.845	0.845	16.8	2.24	0	0.931	8.4
Beryllium	<0.002	<0.002	<0.002	NA	<0.002	NA	<0.002	NA
Cadmium	1.273	<0.005	<0.005	>99.6	<0.006	>99.5	<0.005	>99.6
Chromium	0.687	0.267	0.267	61.1	0.119	82.7	0.354	48.5
Copper	0.063	0.080	0.080	0	0.094	0	0.081	0
Lead	0.100	0.036	0.036	64.0	0.046	54.0	0.252	0
Mercury	<0.0002	<0.0002	<0.0002	NA	<0.0002	NA	<0.0002	NA
Nickel	0.512	0.045	0.045	91.2	0.022	95.7	0.044	91.4
Selenium	<0.005	<0.005	<0.005	NA	<0.005	NA	<0.005	NA
Silver	<0.010	<0.010	<0.010	NA	<0.010	NA	<0.010	NA
Thallium	<0.005	<0.005	<0.005	NA	<0.005	NA	<0.005	NA
Vanadium	<0.010	<0.010	<0.010	NA	<0.011	NA	<0.010	NA
Zinc	0.337	0.036	0.036	89.3	0.035	89.6	0.033	90.2

* Data presented and percent reduction calculated are based on the average concentration of three replicate samples.

† Not applicable. Percent reduction cannot be calculated when analyte is not detected in untreated soil.

TABLE 5. CONCENTRATIONS OF METALS AND ORGANICS IN TCLP OF LEACHATES TREATED AND UNTREATED ALIQUOTS OF SYNCON RESINS SOIL AND CORRESPONDING PERCENT REDUCTION VALUES*

Analyte	Untreated soil		Treated soil					
	Conc., mg/L		Portland cement		Lime/fly ash		Kiln dust	
	Conc., mg/L		Conc., mg/L	% reduction	Conc., mg/L	% reduction	Conc., mg/L	% reduction
Antimony	<0.060		<0.060	NA [†]	<0.060	NA	<0.060	NA
Arsenic	1.007		0.033	96.7	0.019	98.1	0.016	98.4
Barium	1.007		1.847	0	1.107	0	1.39	0
Beryllium	<0.002		<0.002	NA	<0.002	NA	<0.002	NA
Cadmium	0.006		<0.005	>16.7	<0.005	>16.7	<0.005	>16.7
Chromium	0.014		0.016	0	0.025	0	0.010	28.6
Copper	0.116		0.194	0	0.378	0	0.258	0
Lead	0.092		<0.008	>91.3	0.071	22.8	0.101	0
Mercury	<0.0002		<0.0002	NA	<0.0002	NA	<0.0002	NA
Nickel	0.052		0.045	13.5	0.025	51.9	0.022	57.7
Selenium	<0.005		<0.005	NA	<0.005	NA	<0.005	NA
Silver	<0.010		<0.010	NA	<0.010	NA	<0.010	NA
Thallium	<0.005		<0.005	NA	<0.005	NA	<0.005	NA
Vanadium	0.018		<0.010	>44.4	<0.010	>44.4	<0.010	>44.4
Zinc	1.07		0.061	94.3	0.020	98.1	0.043	96.0

(continued)

TABLE 5 (continued)

Analyte	Untreated soil Conc., mg/L	Treated soil				
		Portland cement		Lime/fly ash		Kiln dust
		Conc., mg/L	% reduction	Conc., mg/L	% reduction	Conc., mg/L % reduction
Lindane, µg/liter	<0.5	<0.25	NA	<0.12	NA	<0.10 NA
DDT, µg/liter	<2.2	<0.40	NA	<0.23	NA	<0.20 NA
DDE, µg/liter	<1.07	<0.50	NA	<0.23	NA	<0.20 NA
DDB, µg/liter	7.8	0.38	95.1	<0.23	97.0	<0.55 92.9
PCDF, ng/liter	<4.84 ^{††}	<6.46 ^{††}	NA	<15.7 ^{††}	NA	<5.32 ^{††} NA

* Data presented and reduction efficiencies calculated are based on the average concentration of three replicate samples.

† Not applicable. Cannot calculate percent reduction when analyte is not detected in untreated soil.

†† Average concentration of four replicate samples.

where

- a = pollutant concentration (e.g., mg/L) in TCLP extract of treated sample
- b = pollutant concentration (e.g., mg/L) in TCLP extract of untreated sample
- c = percent removal

The "percent reduction" value indicates the stabilization efficiency; i.e., how effectively the stabilization treatment sequestered or bound the pollutant, thereby yielding a TCLP leachate with a lowered concentration of the pollutant. Note that no correction was made for dilution by addition of binder and water.

The Tri-State Metals Plating soil had detectable concentrations of 7 of the 15 metals analyzed for (barium, cadmium, copper, lead, nickel, chromium, and zinc). Reduction efficiency cannot be calculated for any analyte not detected in the untreated TCLP extract; therefore, reduction efficiencies are reported only for these seven metals. Stabilization/solidification was effective on cadmium (greater than 99.5 percent reduction), nickel (greater than 91.2% reduction), and zinc (greater than 89.3% reduction). The data indicate that reduction efficiencies did not vary significantly with the binders used on these three metals. Reduction efficiencies reported for chromium and lead varied among binders. Lime/fly ash was most effective in stabilizing chromium (82.7%), followed by portland cement (61.1%), and kiln dust (48.5%). Portland cement was most effective in stabilizing lead (64.0%), followed by lime/fly ash with 54.0 percent; no reduction was experienced with the kiln dust binder. All three binders were ineffective in stabilizing barium and copper. Actually, the binders themselves contribute a significant concentration of barium to the extracts. Also, compared with the total metal analyses shown in Table 2, only very small quantities of metals are leaching from the untreated soil.

The Syncon Resins soil had concentrations of 9 of the 15 metals analyzed for (arsenic, barium, cadmium, chromium, copper, lead, nickel, vanadium, and zinc). The untreated TCLP extract concentrations of cadmium, chromium, and vanadium were so low that conclusions cannot be drawn from the available data as to the effectiveness of the stabilization/ solidification process. Stabilization/solidification was effective, however, on arsenic (greater than 96.7%) and zinc (greater than 94.3%). The data indicate that reduction efficiencies did not vary significantly among the binders on these metals. Reduction efficiencies reported for lead and nickel did vary among binders. Portland cement was most effective in stabilizing lead (greater than 91.3%), followed by lime/fly ash (22.8%); kiln dust showed no reduction. Kiln dust was the most effective in stabilizing nickel (57.7%), followed by lime/fly ash (51.9%); portland cement demonstrated only 13.5 percent reduction. All three binders were ineffective in stabilizing barium and copper. Again, all three binders actually contribute a significant concentration of barium to the extracts. Also, compared with the total metal concentration present (as shown in Table 1), only very small quantities of metals were leaching from the untreated soil.

Four pesticides were analyzed for in the untreated and treated Syncon Resins TCLP extracts: lindane (gamma-BHC), DDT, DDE, and DDD. Because lindane was not detected in the untreated TCLP extract, reduction efficiencies could not be calculated. In the case of DDT and DDE, mixed data were obtained on the untreated TCLP extracts, which makes it difficult to draw any conclusions as to the effectiveness of the stabilization/solidification process. Triplicate samples of the untreated soil for DDT and DDE showed nondetected, estimated concentrations below the detection limit, and low detected concentrations. Based on these results, reduction efficiencies cannot be calculated for DDT and DDE. Reduction efficiencies reported for DDD were 97.0, 95.1, and 92.9 percent for lime/fly ash, portland cement, and kiln dust, respectively.

The TCLP analyses for four replicate untreated Syncon Resins soil indicated that furans (PCDF) were not detected in three of the four samples and detected at 10.7 ng/L in the fourth sample. As was the case with several of the metals, lindane, DDT, and DDE, the reduction efficiency of a pollutant that is not detected in the untreated sample TCLP extract cannot be calculated.

COMPARISON OF SARM AND SUPERFUND SOIL TCLP ANALYTICAL RESULTS

A second objective of this project was to compare analytical results obtained during Phase I on synthetic soil with results obtained during Phase II on Superfund soil. To arrive at a valid comparison of these results, one must review data on similarly contaminated soils. A review of the analytical data on the SARM soil and the soil from Tri-State Metals Plating and Syncon Resins indicated that the SARM II (Table 6) and the Syncon Resins soils (Table 1) were the most similar for purposes of a performance comparison.

Tables 7, 8, and 9 present TCLP analytical results for the untreated and treated SARM II and Syncon Resins soils with the binders portland cement, lime/fly ash, and kiln dust, respectively. These tables also present reduction efficiencies to permit a comparison of the effectiveness of stabilization/solidification on SARM II and Syncon Resins soil for specific analytes and binders. The TCLP extract analytes in common in both the SARM II soil and the Syncon Resins soil were arsenic, cadmium, chromium, copper, lead, nickel, and zinc. As shown in Table 7, with portland cement as the binder, similar reduction efficiencies were obtained for lead (78.6% vs. 91.2%) and zinc (96.3% vs. 94.3%); however, very dissimilar reduction efficiencies were obtained for copper (93.2% vs. 0%) and nickel (90.0% vs. 12.6%). Arsenic and chromium reduction efficiencies could not be compared because these metals were not detected in the untreated SARM II soil, and cadmium reduction efficiencies could not be compared because of the low concentration in the Syncon Resins untreated soil.

Results obtained with lime/fly ash (Table 8) indicate that reduction efficiencies for zinc (99.9% vs. 98.1%) compare well; however, results for other analytes such as copper (96.6% vs. 0%), lead (>78.6% vs. 22.6%), and nickel (>90.0% vs. 51.7%) were not comparable. As with portland cement, arsenic, cadmium, and chromium reduction efficiencies could not be compared.

Kiln dust reduction efficiencies (Table 9) demonstrate that results obtained for zinc compare well (94.6% vs. 96.0%); however, reduction efficiencies for copper (89.9% vs. 0%), lead (47.1% vs. 0%), and nickel (>90.0% vs. 57.2%) were very dissimilar. As with portland cement and lime/fly ash, reduction efficiencies for arsenic, cadmium, and chromium could not be compared.

TABLE 6. RESULTS OF TOTAL WASTE ANALYSIS FOR SARM SAMPLES*

Analyte	SARM 1 High organic, low metal	SARM 2 Low organic, low metal	SARM 3 Low organic, high metal	SARM 4 High organic, high metal
<u>Volatiles, µg/kg</u>				
Acetone	3,150	230	220	13,000
Chlorobenzene	330	9.2	8.9	270
1,2-dichloroethane	380	3.9	3.1	830
Ethylbenzene	3,350	74	100	2,500
Styrene	1,000	26	24	540
Tetrachloroethylene	710	16	13	540
Xylene	4,150	210	150	3,700
<u>Semivolatiles, µg/kg</u>				
Anthracene	940	275	265	775
Bis(2-ethylhexyl) phthalate	600	34	140	500
Pentachlorophenol	135	62	15	78
<u>Inorganics, mg/kg</u>				
Arsenic	18	18	904	810
Cadmium	17	23	1,280	1,430
Chromium	27	37	1,190	1,650
Copper	193	260	9,650	13,300
Lead	190	240	15,200	16,900
Nickel	27	32	1,140	1,380
Zinc	392	544	53,400	28,900

* Source: Weitzman, L., and L. E. Hamel. Evaluation of Solidification/Stabilization as a BDAT for Superfund Soils. Acurex Corporation. EPA Contract No. 68-03-3241, September 1988.

TABLE 7. COMPARISON OF THE EFFECTIVENESS OF PORTLAND CEMENT AS BINDER IN SARM II SOIL VERSUS SYNCON RESINS SOIL (TCLP data reported in mg/L)

Analyte	SARM II			Syncon Resins		
	Untreated	Treated B/S = 0.7	% reduc- tion	Untreated	Treated B/S = 0.5	% reduc- tion
Arsenic	ND* (0.15)	ND (0.15)	NA†	1.007	0.0331	96.7
Cadmium	0.73	ND (0.01)	>98.6	0.0062	ND (0.005)	>19.4
Chromium	ND (0.01)	0.03	NA	0.0143	0.0156	0
Copper	0.89	0.06	93.2	0.116	0.194	0
Lead	0.70	0.15	78.6	0.092	0.0081	91.2
Nickel	0.40	0.04	90.0	0.0516	0.0451	12.6
Zinc	14.6	0.54	96.3	1.070	0.0614	94.3

* Not detected at concentration indicated in parentheses.

† Not applicable when analyte is not detected in untreated material.

TABLE 8. COMPARISON OF THE EFFECTIVENESS OF LIME/FLY ASH AS BINDER IN SARM II SOIL VERSUS SYNCON RESINS SOIL (TCLP data reported in mg/L)

Analyte	SARM II			Syncon Resins		
	Untreated	Treated B/S = 2.0	% reduc- tion	Untreated	Treated B/S = 0.5	% reduc- tion
Arsenic	ND* (0.15)	ND (0.15)	NA†	1.007	0.0186	98.2
Cadmium	0.73	ND (0.01)	>98.6	0.0062	ND (0.005)	>19.4
Chromium	ND (0.01)	ND (0.01)	NA	0.0143	0.0246	0
Copper	0.89	0.03	96.6	0.116	0.378	0
Lead	0.70	ND (0.15)	>78.6	0.092	0.0712	22.6
Nickel	0.40	ND (0.04)	>90.0	0.0516	0.0249	51.7
Zinc	14.6	0.02	99.9	1.070	0.0198	98.1

* Not detected at concentration indicated in parentheses.

† Not applicable when analyte is not detected in untreated material.

TABLE 9. COMPARISON OF THE EFFECTIVENESS OF KILN DUST
AS BINDER IN SARM II SOIL VERSUS SYNCON RESINS SOIL
(TCLP data reported in mg/L)

Analyte	SARM II			Syncon Resins		
	Untreated	Treated B/S = 1.0	% reduc- tion	Untreated	Treated B/S = 0.75	% reduc- tion
Arsenic	ND* (0.15)	ND (0.15)	NA†	1.007	0.0165	98.4
Cadmium	0.73	ND (0.01)	>98.6	0.0062	ND (0.005)	>19.4
Chromium	ND (0.01)	0.05	NA	0.0143	0.0105	26.6
Copper	0.89	0.09	89.9	0.116	0.258	0
Lead	0.70	0.37	47.1	0.092	0.101	0
Nickel	0.40	ND (0.04)	>90.0	0.0516	0.0221	57.2
Zinc	14.6	0.78	94.6	1.070	0.0431	96.0

* Not detected at concentration indicated in parentheses.

† Not applicable when analyte is not detected in untreated material.

CONCLUSIONS

The results of this study indicate that the stabilization/solidification process can effectively stabilize Superfund soils containing arsenic, cadmium, nickel, zinc, and the pesticide DDD when portland cement, lime/fly ash, or kiln dust is used as the binder. Stabilization efficiencies for these metals ranged from >89.3 percent for zinc to >99.5 percent for cadmium. The stabilization efficiency obtained for DDD was 97.0 percent with lime/fly ash as the binder. A comparison of total waste analyses with TCLP for untreated soil shows that only a small portion of the total contaminants leaches from the soil.

The binder selection had a great impact on the stabilization efficiencies of some metals, e.g., chromium, lead, and nickel. Lime/fly ash proved to be the most effective binder for stabilizing chromium in the Tri-State Metals soil, with an 82.7 percent reduction efficiency, whereas portland cement and kiln dust stabilized only 61.1 and 48.5 percent, respectively. Portland cement was the most effective binder for treating lead (64.0% removal), followed by lime/fly ash (54.0%). No stabilization was experienced with kiln dust. Tri-State Metals Plating soil is described as a loamy, glacial till outwash soil over sand and gravel.

Portland cement proved to be the most effective binder for stabilizing lead in the Syncon Resins soil with a stabilization efficiency of greater than 91.3 percent; lime/fly ash and kiln dust were ineffective. Kiln dust, however, was the most effective binder for stabilizing nickel in the Syncon Resins soil, followed closely by lime/fly ash; stabilization efficiencies were 57.7 and 51.9 percent, respectively. Portland cement was ineffective in stabilizing nickel in the Syncon Resins soil. Syncon Resins soil is described as unconsolidated, consisting primarily of alluvial sand, silt, clay, and detritus.

Results on both the Syncon Resins and Tri-State Metals Plating soils indicate that all three binders were ineffective in stabilizing copper.

It was impossible to report stabilization efficiencies for a number of metals, pesticides, and polychlorinated dibenzofurans analyzed under this study because the untreated TCLP extract concentrations were below detectable limits.

From an operational standpoint, several conclusions can be drawn. Overall, the portland cement binder performed the best by yielding a soil/binder product exceeding 250 psi, which is the upper limit of measurement with the available testing equipment. This was true for both Syncon Resins and Tri-State Metals Plating soils and for all binder-to-soil ratios (0.5, 0.75, and 1.0). The lime/fly ash binder performed almost as well on the Tri-State soil. On the Syncon Resins soil, this binder produced a nearly linear rise in compressive strength from 50 to 250 psi with increasing

binder-to-soil ratios. The kiln dust binder performed the least well; the unconfined compressive strength of the highest binder-to-soil ratio barely met the minimum acceptable level of 50 psi.

The following are some additional specific conclusions drawn from the use of stabilization/solidification for treatment of Syncon Resins and Tri-State Metals Plating soils:

Syncon Resins Soil--

° Portland cement binder

- 1) Uniform blends with good compressive strength were achieved at the lowest binder-to-soil (B/S) ratios.
- 2) Desired product was achieved throughout the 0.3 to 0.4 water-to-total solids (W/TS) ratios, although the 0.4 blend had free-standing liquid at the 0.5 B/S ratio.
- 3) Use of a 0.3 W/TS ratio is recommended to ensure cohesive mixing of soil and to prevent solids from settling.

° Kiln dust

- 1) Textured blends were achieved with moderate, slow-developing, compressive strength.
- 2) Desired product was achieved at 0.38 to 0.4 W/TS ratio, but compressive strength did not increase significantly with increasing B/S ratios.
- 3) Use of a 0.4 W/TS ratio is recommended to enhance blend homogeneity.

° Lime/fly ash mixture

- 1) Problems were encountered in achieving uniform blends; thorough mixing was not always effective.
- 2) Acceptable product was achieved at 0.4 to 0.48 W/TS ratios.
- 3) Compressive strength was achieved faster at the higher B/S ratios.
- 4) Use of a 0.45 W/TS ratio is recommended to enhance the thoroughness of mixing.

Tri-State Metals Plating--

° Portland cement

- 1) Uniform hydrated appearance was achieved at a W/TS ratio as low as 0.2.
- 2) Desired product was achieved throughout the 0.2 to 0.4 W/TS range.
- 3) All blends achieved greater than 50 psi compressive strength after 24 hours.
- 4) Use of a 0.3 W/TS ratio is recommended to enhance mixing.

° Kiln dust

- 1) Thoroughness of blending is the key factor in achieving uniform blend product.
- 2) Compressive strength of 50 psi was achieved in 0.2 to 0.4 W/TS range.
- 3) Use of a 0.4 W/TS ratio is recommended to ensure thorough blending.

° Lime/fly ash mixture

- 1) Blends achieved uniform silty, monolithic product.
- 2) Desired product was achieved with 0.2 to 0.4 W/TS blends.
- 3) All blends achieved greater than 50 psi compressive strength after 48 hours.
- 4) Use of a 0.4 W/TS ratio is recommended to enhance thoroughness of mixing.

For a comparison of pollutant stabilization efficiencies obtained with the SARM soil and those obtained with actual Superfund soil, the selected SARM and Superfund soils had to have a similar chemical and physical composition. A review of the available data indicated that SARM II (low metals, low organics) and Syncon Resins soils were most similar. The stabilization tests indicated that the SARM II soil and Syncon Resins soil exhibited similar stabilization efficiencies for zinc regardless of which binder was used. Stabilization efficiencies for lead were similar when portland cement was used as the binder. The stabilization efficiencies for other metals (e.g., copper and nickel) were very dissimilar when portland cement, lime/fly ash, and kiln dust were used as binders. Stabilization efficiencies for lead were also dissimilar when lime/fly ash and kiln dust were used.

It is apparent from the data presented in this study that the stabilization/solidification process could not be evaluated to its full potential. A number of analytes were not detected or were at too low a concentration for stabilization efficiencies to be calculated. In future treatability studies, it is recommended that the investigator spike the untreated soil with the compounds of interest in concentrations that will test the limitation of the technology as opposed to the limitation of the analytical methodology.

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TREATABILITY OF TRIBUTYLTIN IN POTWS

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ABSTRACT

Organotin contaminated wastewater generated during drydock and ship cleaning operations must be treated before discharge to the environment. A study was conducted to assess the treatability of tributyltin in a conventional primary/activated sludge municipal wastewater treatment plant. Experiments were conducted to evaluate the treatability and fate of tributyltin by both abiotic and biotic mechanisms.

Sorption isotherms were measured for tributyltin and its degradation products on primary sludge, mixed-liquor solids, and digested sludge. Partition coefficients ranged from 1,585 to 13,200 for monobutyltin and tributyltin, respectively. The organotin compounds were not removed by stripping.

Both aerobic and anaerobic biotic mechanisms were studied for degradation of tributyltin. Steady state aerobic degradation levels in the range of 75-95% were observed with sludge retention times of 8 and 18 days. In anaerobic studies, biological methane potential and anaerobic toxicity assays showed no effect on the performance of methanogens.

INTRODUCTION

Tributyltin (TBT) is used as an antifouling toxicant in boat paints and as wood preservative, molluscicide and insecticide. It has become popular because of its excellent antifouling properties, long life-time, and lack of corrosion problems. During the life cycle of paints TBT is slowly released to the aqueous environment. During drydock and ship cleaning activities wastewater streams contaminated with TBT are produced. Treatment is desirable before the wastewaters are discharged to the environment.

Physical-chemical and biological treatment processes are available for treatment of organotin-contaminated wastewaters. In general, biological processes are more economical and easier to apply. However, since TBT and its degradation products are acutely toxic to many microorganisms, mollusks, insects, and higher plants (1,2), treatability studies were undertaken to assess the potential of publicly-owned treatment works (POTWs) to remove organotin compounds. Treatment of TBT-contaminated wastewater at municipal wastewater treatment plants is advantageous for the following reasons: (1) POTWs are readily available all over the country, (2) substantial dilution is available which minimizes toxic impacts of TBT compounds, (3) a diverse biomass is available which enhances the potential for degradation of toxic compounds, and (4) nutrients and co-metabolites required for successful operation of biological processes are present.

Studies in the literature suggest that biodegradation of organotin compounds occurs and is a major degradation pathway in aquatic and sedimentary environments. Degradation of TBT in soil has been reported (3). The effects of organotin-contaminated wastewater on the activated sludge process was studied using continuous bench-scale reactors and fish bioassays (4). Performance and stability of a municipal treatment facility treating organotin concentrations up to 75 $\mu\text{g/L}$ demonstrated that the full-scale activated sludge process was not adversely affected by the contaminant (5). None of the studies characterized the tributyltin fate or specification in the activated sludge process.

The present study was conducted in three phases. In the first phase analytical methodology to recover TBT and related compounds from both sludge and aqueous matrices was investigated. The second phase assessed the role of abiotic mechanisms (stripping and sorption) on removal of TBT. The final phase evaluated both aerobic and anaerobic mechanisms of biodegradation.

ANALYTICAL METHODOLOGY

Analytical methods used in the studies cited did not allow determination of degradation and ultimate fate of organotin compounds during treatment by the activated sludge process. Recent advances in analytical techniques have made this possible. The analytical method used in the present study was a modification of techniques described by Matthias (6) and Muller (7). The basic methods described were based on simultaneous hybridization/extraction with gas chromatography flame photometric detection. Application of the

method to raw wastewater or sludge samples resulted in severe emulsion problems. The modification used in the present study included a sonification step on the combined extracts to break the solvent-water emulsion prior to drying with sodium sulfate. Sodium borohydride was used for hybridization and methylene chloride was used as the extracting solvent. Di-n-propyltin-dichloride or diphenyltin dichloride was used as an internal standard.

EXPERIMENTAL RESULTS AND DISCUSSION

ABIOTIC STUDIES (STRIPPING)

The major abiotic mechanisms for removal of most organic compounds in conventional primary/activated sludge wastewater treatment plants are volatilization (surface desorption) or air stripping and sorption on solids and sludges.

In order to assess the fate of a particular tributyltin derivation in wastewater one must consider the dissociated active form, the TBT cation (Bu_3Sn^+) and its major metabolites presumably formed by progressive debutylation to inorganic tin (i.e., tributyltin (TBT) $\text{Bu}_3\text{Sn}^+ \rightarrow$ dibutyltin (DBT) $\text{Bu}_2\text{Sn}^{2+} \rightarrow$ monobutyltin (MBT) $\text{BuSn}^{3+} \rightarrow$ inorganic tin Sn^{4+}).

Although these cationic species are not expected to be affected by the volatilization or air stripping mechanisms, tests were conducted in bubble columns to validate this assumption. Two one-liter bubble columns (length to diameter ratio = 12) similar to the design of Mackay (8) were acid washed, rinsed thoroughly, and filled with a solution containing 0.5 mg/L of tributyltin chloride, dibutyltin dichloride, and monobutyltin trichloride - after 20 hours the columns were dumped and refilled with the same test solution in an attempt to eliminate glass surface adsorption during the experimental run. Nitrogen from a cylinder was passed through a pressure regulator, flow controller, gas saturation bottle and into the bottom of the fritted bubble column. Nitrogen was used as the stripping gas to avoid the possibility of air oxidation. Flow rate was measured at 70 mL/minute with a soap bubble flow meter. The column was maintained at 23°C with a water jacket. Stripping was continued over a 20-hour period. Samples were withdrawn from the column for analyses at 0, 4, 13, and 20 hours. Analytical data are summarized in Table 1.

TABLE 1. STRIPPING DATA FOR ORGANOTINS

Time (hr)	TBT (mg/L)	DBT (mg/L)	MBT (mg/L)
0	0.50	0.52	0.51
4	0.47	0.49	0.49
13	0.47	0.48	0.49
20	0.45	0.47	0.47
TBT=tributyltin DBT=dibutyltin MBT=monobutyltin			

Stripping data in Table 1 have shown that TBT and its degradation products are nonvolatile. The observed small changes in concentration with time are most likely due to continued adsorption of the organotins on the walls of the glass bubble column.

ABIOTIC STUDIES (MEASUREMENT OF SORPTION ISOTHERMS)

In dilute systems typical of most environmental situations, the partition coefficient K_p for sorption on wastewater solids can be defined as follows:

$$K_p = C_s/C_L \quad (1)$$

where: C_s = concentration of pollutant in the solid phase and C_L = concentration of pollutant in the liquid phase.

The usual method for measuring partition coefficients is to determine a sorption isotherm. Slurries of the wastewater solids are prepared in different initial concentrations of the toxic organic chemical being studied. After the systems reach equilibrium, the concentration in both the solution and solid phases are measured (solid phase concentration can be calculated based on the difference between the initial concentration added and the solution concentration at equilibrium). Data are fitted to the Freundlich equation which can be written:

$$X/M = KC_e^n \quad (2)$$

where: X = $C_o - C_e$ which is the amount of solute sorbed from a given volume of solution

C_o = initial concentration of solute added

C_e = concentration of solute at equilibrium

M = weight of solids added to the solution

K and n = empirical constants

Data are fitted to the logarithmic form of Equation (2) which can be written as follows:

$$\log X/M = \log K + n \log C_e \quad (3)$$

For dilute solutions this equation yields a straight line with a slope of n and an intercept equal to the value of K (X/M at $C_e = 1.0$) when X/M is plotted as a function of C_e on logarithmic paper. The intercept is an indicator of sorption capacity and the slope of sorption intensity. K is often referred to as the sorption or adsorption coefficient. To obtain the partition coefficient (K_p) when X/M is in mg/gm and C_e is in mg/L, the following equation is used:

$$K_p = \frac{X/M}{C_e/1000} \quad (4)$$

(Equation (4) also applies when X/M is in $\mu\text{g/gm}$ and C_e is in $\mu\text{g/L}$).

A detailed experimental protocol for determination of the partition coefficient or sorption capacity of wastewater solids for toxic organic

compounds has been described previously (9). The moisture content of the wastewater solids was determined by drying a portion to constant weight at 110°C. A stock slurry that contained distilled water and wastewater solids was prepared to give the desired concentration of solids for the isotherm test. Sludge slurries were transferred to 500 ml bottles to yield 0.2 g dry organic solids per liter. Organotin compounds were dosed at 10, 50, 200, 500, and 1,000 µg/L initial concentration for primary, mixed-liquor, and digested sludge. Bottles were capped and stirred for 18 hours. The phases were separated via centrifugation and aqueous and solid phases analyzed by the analytical method described earlier. Sorption data for TBT, DBT, and MBT are shown in Tables 2-4.

TABLE 2. SORPTION DATA FOR TRIBUTYL TIN

Type of Sludge	C _o µg/L	C _e µg/L	X µg/L	X/M µg/g	log K _p	Avg. log K _p
Primary sludge	10.0	3.0	7.0	35.0	4.07	4.07
	50.0	13.0	37.0	185.0	4.15	
	200.0	71.0	129.0	645.0	3.96	
	500.0	106.0	394.0	1970.0	4.27	
	1000.0	398.0	602.0	3010.0	3.88	
Mixed Liquor Sludge	10.0	5.0	5.0	25.0	3.70	3.92
	50.0	21.0	29.0	145.0	3.84	
	200.0	54.0	146.0	730.0	4.13	
	500.0	120.0	380.0	1900.0	4.20	
	1000.0	487.0	513.0	2565.0	3.72	
Digested sludge	10.0	3.0	7.0	35.0	4.07	4.12
	50.0	20.0	30.0	150.0	3.88	
	200.0	39.0	161.0	805.0	4.31	
	500.0	98.0	402.0	2010.0	4.31	
	1000.0	313.0	687.0	3435.0	4.04	

TABLE 3. SORPTION DATA FOR DIBUTYL TIN

Type of Sludge	C_o $\mu\text{g/L}$	C_e $\mu\text{g/L}$	X $\mu\text{g/L}$	X/M $\mu\text{g/g}$	$\log K_p$	Avg. $\log K_p$
Primary sludge	10.0	6.0	4.0	20.0	3.52	3.58
	50.0	33.0	17.0	85.0	3.41	
	200.0	80.0	120.0	600.0	3.88	
	500.0	296.0	204.0	1020.0	3.54	
	1000.0	596.0	404.0	2020.0	3.53	
Mixed Liquor sludge	10.0	4.0	6.0	30.0	3.88	3.72
	50.0	31.0	19.0	95.0	3.49	
	200.0	110.0	90.0	450.0	3.61	
	500.0	148.0	352.0	1760.0	4.08	
	1000.0	595.0	405.0	2025.0	3.53	
Digested sludge	10.0	5.0	5.0	25.0	3.70	3.48
	50.0	29.0	21.0	105.0	3.56	
	200.0	160.0	40.0	200.0	3.10	
	500.0	325.0	175.0	875.0	3.43	
	1000.0	547.0	453.0	2265.0	3.62	

TABLE 4. SORPTION DATA FOR MONOBUTYL TIN

Type of sludge	C_o $\mu\text{g/L}$	C_e $\mu\text{g/L}$	X $\mu\text{g/L}$	X/M $\mu\text{g/g}$	$\log K_p$	Avg. $\log K_p$
Primary sludge	10.0	7.0	3.0	15.0	3.33	3.31
	50.0	30.0	20.0	100.0	3.52	
	200.0	161.0	39.0	195.0	3.08	
	500.0	360.0	140.0	700.0	3.29	
	1000.0	709.0	291.0	1455.0	3.31	
Mixed Liquor Sludge	10.0	6.0	4.0	20.0	3.52	3.48
	50.0	33.0	17.0	85.0	3.41	
	200.0	77.0	123.0	615.0	3.90	
	500.0	320.0	180.0	900.0	3.45	
	1000.0	793.0	207.0	1035.0	3.12	
Digested sludge	10.0	8.0	2.0	10.0	3.10	3.20
	50.0	32.0	18.0	90.0	3.45	
	200.0	173.0	27.0	135.0	2.89	
	500.0	361.0	139.0	695.0	3.28	
	1000.0	726.0	274.0	1370.0	3.28	

All the organotin compounds showed strong sorption characteristics. Average $\log K_d$ values were 4.04 ± 0.10 for TBT; 3.59 ± 0.12 for DBT; and 3.3 ± 0.14 for MBT for sorption on all three types of wastewater solids tested. The sorption data for TBT on mixed liquor solids from Table 2 is plotted according to the logarithmic form of the Freundlich equation (Equation 3) and is shown in Figure 1.

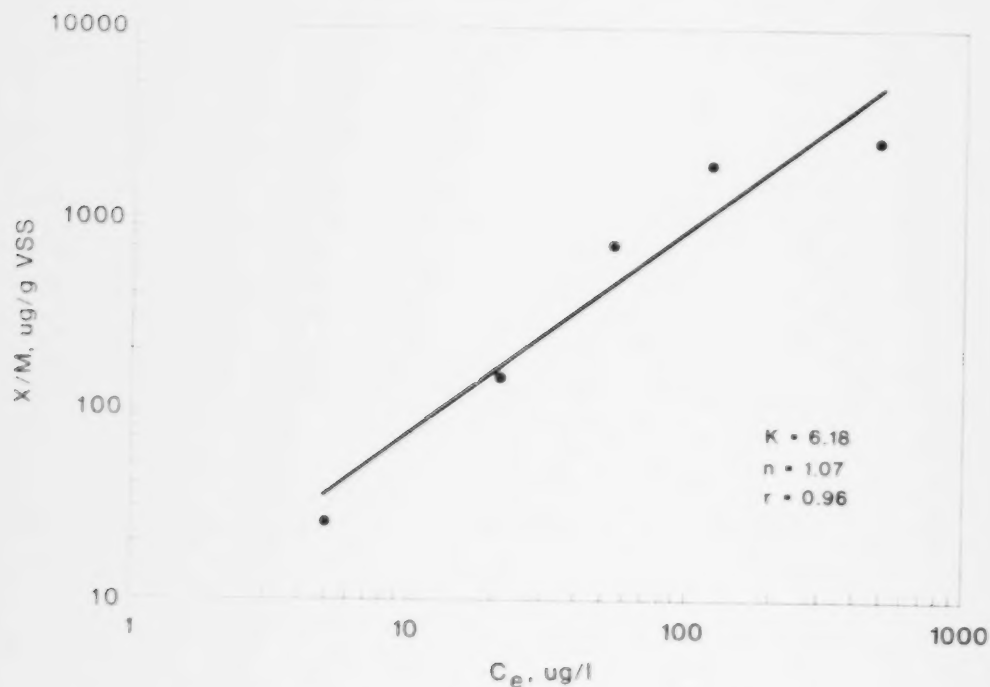


Figure 1. Sorption isotherm for TBT on mixed liquor solids.

The isotherm is typical of those obtained for all the organotin compounds on all three types of wastewater solids studied.

BIOTIC STUDIES (INHIBITION TESTING)

Knowledge of inhibitory characteristics of TBT to the microorganisms is important for determining fate of TBT in activated sludge processes. Electrolytic respirometry studies were used to determine the inhibition characteristics of the compounds under consideration using unacclimated biomass. The studies were conducted using an automated, continuous oxygen uptake measuring Voith, Sapromat B-12 respirometer. The instrument consists of a temperature controlled waterbath, a recorder, and a cooling unit. The waterbath contains the measuring unit shown in Figure 2.

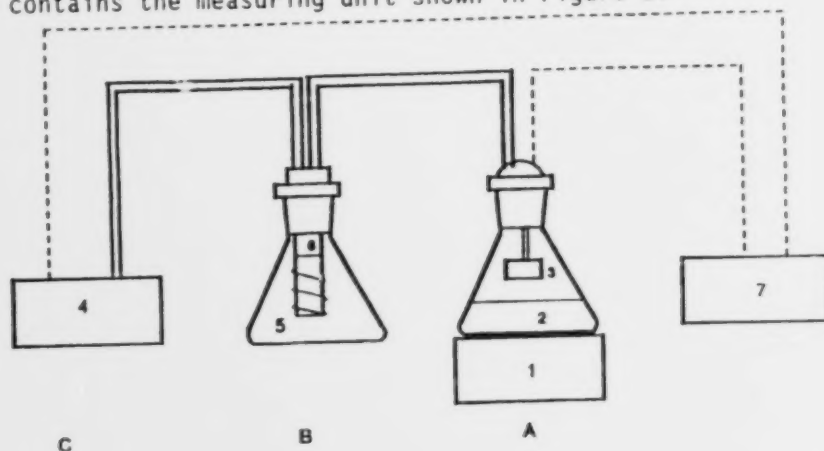


Figure 2. Electrolytic respirometry (measuring unit).

- | | |
|------------------------|-----------------------------|
| A. Reaction vessel. | 1. Magnetic stirrer. |
| B. Oxygen generator. | 2. Sample (250 ml). |
| C. Pressure indicator. | 3. Carbon dioxide absorber. |
| | 4. Pressure indicator. |
| | 5. Electrolyte. |
| | 6. Electrodes. |
| | 7. Recorder. |

The recorder shows the digital indication of oxygen uptake and constructs a graph of these values for each measuring unit. The recorder is also connected to an IBM-AT computer, which collects data every fifteen minutes. The cooling unit constantly recirculates water to maintain constant temperature in the waterbath. Each measuring unit consists of a reactor vessel with a CO₂ absorber mounted in a stopper, an oxygen generator, and a pressure indicator.

This measuring unit is interconnected by tubes, forming an air sealed system, so that the atmospheric pressure fluctuations do not adversely affect the results. The magnetic stirrer ensures effective exchange of gases by providing vigorous agitation. The activity of the microorganisms in the sample creates a vacuum which, via a pressure indicator, triggers the oxygen generator. It supplies the required amount of oxygen by electrolytic dissociation of a copper sulfate solution in 5% sulfuric acid. The quantity of the sample, the amperage for electrolysis, and the speed of the synchronous motor are so adjusted that, with a sample of 250 mL, the digital counter indicates the oxygen uptake directly in mg/L. Carbon dioxide generated is absorbed by soda lime, the nitrogen/oxygen ratio in the gas phase above the sample is maintained throughout the experiment, and there is no depletion of oxygen.

The nutrient solution used in these studies was a synthetic medium formulated by the Organization for Economic Cooperation and Development (OECD) and was prepared from the stock solutions shown in Table 5.

TABLE 5. COMPOSITION OF OECD NUTRIENT SOLUTION FOR ELECTROLYTIC RESPIROMETRY

Stock Solution	Nutrient	Weight/L
A.	KH_2PO_4	8.5 g
	K_2HPO_4	21.75 g
	$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	33.4 g
	NH_4Cl	2.5 g
B.	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	22.5 g
C.	CaCl_2	27.5 g
D.	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.25 g
E.	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	39.9 mg
	H_3BO_3	57.2 mg
	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	42.8 mg
	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$	34.7 mg
	FeCl_3 EDTA	100.0 mg
F.	Yeast Extract	150.0 mg

Nutrient solution prepared by diluting 10 mL A and 1.0 mL B-F to one liter in distilled water.

Aniline, at a concentration of 100 mg/L, was used as the reference substance. The concentrations of tributyltin used for inhibition studies was 50, 100, 500, and 1000 $\mu\text{g/L}$. Tributyltin stock solution was prepared in acetone and the reactor vessels were coated with appropriate amounts of this solution to achieve desired concentration. Acetone was evaporated before adding the nutrient solution and make-up deionized water.

The microbial biomass was activated sludge from the Little Miami wastewater treatment plant in Cincinnati, Ohio, which receives primarily municipal domestic wastewater. The activated sludge sample was brought to an

endogenous phase by aerating for 24 hours. The sludge biomass at 30 mg/L was added to the medium. The synthetic medium was brought to a final volume of 250 mL.

The experimental system for inhibition studies consisted of duplicate flasks for the reference substance aniline, toxicity controls (tributyltin plus aniline at 100 mg/L), and inoculum control. An unacclimated microbiota was used. The contents of the reaction vessels were first stirred for an hour to ensure an endogenous respiration state at the initiation of oxygen uptake measurements. The contents were then transferred to reaction vessels coated with tributyltin and aniline was added. The reaction vessels were incubated at 25°C in the dark, enclosed in the temperature controlled waterbath, and stirred continuously throughout the run.

Oxygen uptake of the reference substance aniline and the toxicity controls, containing tributyltin at four different concentrations, was followed over a period of 7 days. The oxygen uptake data is graphically represented in Figure 3.

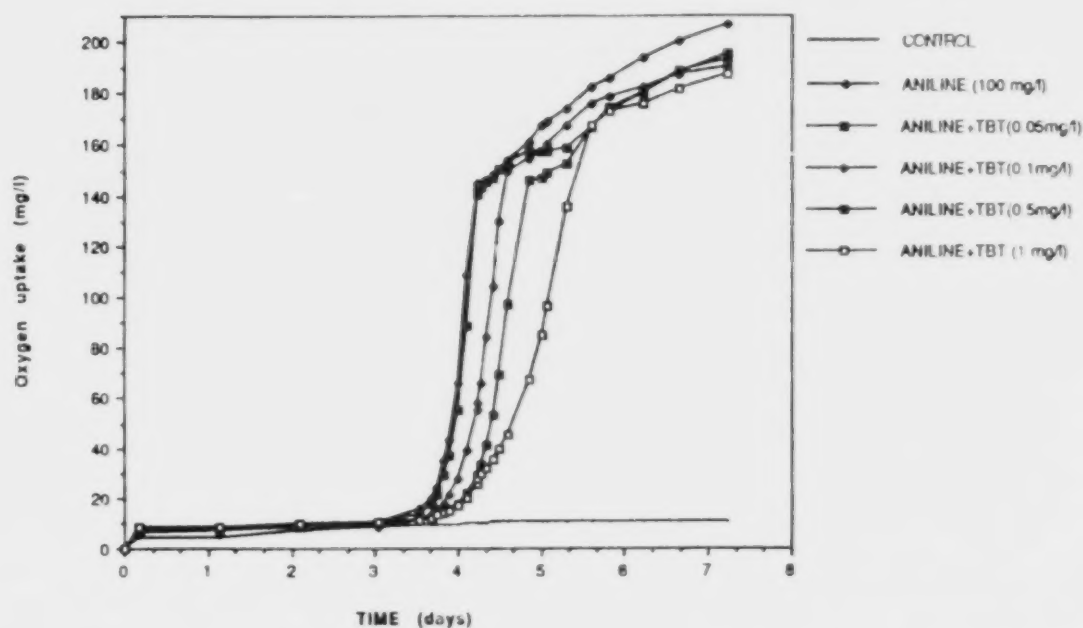


Figure 3. Oxygen uptake data for inhibition studies

Analysis of the culture samples at the end of the respirometric run revealed 80% to 90% degradation of tributyltin. The oxygen uptake data shown in Figure 3 demonstrate that TBT was not inhibitory to the degradation of aniline up to concentrations of 1000 $\mu\text{g/L}$. However, there was an impact on the lag time prior to the onset of degradation which increased with increasing TBT concentrations.

BIOTIC STUDIES (CONTINUOUS FLOW SWISHER REACTORS)

The Swisher reactor simulates the flow pattern of an aeration basin and a clarifier. A schematic diagram of the reactor is shown in Figure 4.

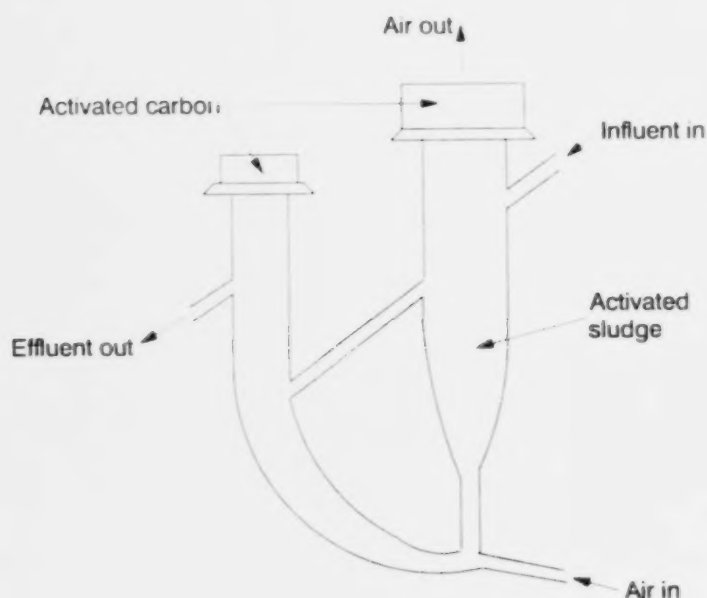


Figure 4. Schematic of Swisher Flow Reactor.

The larger arm contains the biomass which is recycled in the reactor by air introduced in the inlet. The smaller arm acts as a clarifier. A series of 300 mL continuous flow Swisher reactors were set up to investigate the steady state biodegradation of TBT. Sufficient air was introduced to maintain a dissolved oxygen concentration of 3.0 $\mu\text{g/L}$. Influent was pumped to the reactors at a flow rate of 1.2 liters per day resulting in a hydraulic

retention time of 6 hours (liquid volume in the reactor was 200 mL). Solids were wasted at regular intervals to maintain the desired solids retention time (SRT). The reactors were charged with activated sludge from the Mill Creek sewage treatment plant. The units were fed wastewater spiked with TBT at 1.0, 12.5, 50, and 100 $\mu\text{g/L}$. Two wastewater feeds, natural and synthetic, were used. Primary effluent from the Mill Creek treatment facility was used as natural feed and synthetic feed was prepared in the laboratory. Composition of the synthetic feed is given in Table 6.

TABLE 6. COMPOSITION OF SYNTHETIC FEED FOR CONTINUOUS SWISHER FLOW REACTORS

Bottle	Chemical	Concentration (g/L)	Volume added (mL)
B1	Phosphate Buffer		20.0
	NH_4Cl	1.7	
	KH_2PO_4	8.5	
	K_2HPO_4	21.75	
	Na_2HPO_4	33.4	
B2	Magnesium sulfate	22.5	20.0
B3	Calcium chloride	36.0	20.0
B4	Ferric chloride	0.25	20.0
B5	Sodium bicarbonate	75.0	80.0
B6	Organics		20.0
	Yeast extract	55.0	
	Bactopeptone	50.0	
	Meat extract	50.0	
B7	Urea	50.0	20.0
B8	Fish meal	50.0	10.0

The above chemicals were added to four liters of distilled water to form synthetic feed to the Swisher flow reactors.

Mixed liquor volatile suspended solids, chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), total organic carbon, ammonia nitrate, and nitrite were measured to document proper operation of the continuous flow reactors. The experiment was conducted at two SRTs (8 and 18 days). Samples were analyzed for TBT and its degradation compounds to evaluate the acclimation and steady-state performance of the continuous flow reactors. Results obtained at steady state are presented in Table 7.

TABLE 7. STEADY STATE DEGRADATION OF TBT IN CONTINUOUS FLOW SWISHER REACTORS

Feed type	Initial Conc. TBT, $\mu\text{g/L}$	Percent Biodegradation	
		8 day SRT	18 day SRT
Natural	100	63.1 ± 2.5	86.0 ± 2.0
	50	72.3 ± 4.4	97.0 ± 3.0
	12.5	72.0 ± 12.5	89.5 ± 8.0
	1.0	75.0 ± 10.0	98.0 ± 2.0
Synthetic	100	83.4 ± 2.0	90.0 ± 2.5
	50	94.9 ± 4.0	95.0 ± 4.0
	12.5	83.0 ± 8.8	94.5 ± 4.0
	1.0	85.0 ± 15.0	88.9 ± 11.0

Steady state degradation data in Table 7 for the continuous flow Swisher reactor demonstrate that substantial biodegradation was achieved with both natural and synthetic wastewater feeds. Biodegradation increased with the longer SRT. The major biodegradation product was MBT with lesser amounts of DBT. Mass balance calculations indicated inorganic tin was also produced.

BIOTIC STUDIES (SHAKER FLASK EXPERIMENTS)

Initially an attempt was made to measure the kinetics of the TBT degradation reaction using electrolytic respirometry. TBT at 10, 20, and 30 mg/L was added to the reaction flasks. Microbiota used was taken from the continuous flow Swisher reactors. After 7 days in the run no biological activity was observed in the respirometric flasks. As a result kinetic data were determined in shaker flask studies. These studies were conducted by contacting TBT at desired concentrations with the acclimated biomass in a batch mode and determining the change in concentration of TBT with time.

In the experiments, 250 mL flasks were filled with 100 mL of feed (synthetic and natural wastewater separately), spiked with 50 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ of TBT. Acclimated biomass from Swisher reactors was then added to the flasks. Actual concentrations were determined at zero time by analyzing the contents of the flasks. The flasks were then analyzed at varying times for TBT and its degradation products.

The biokinetic constants were determined assuming a constant biomass concentration. This assumption is reasonable on the basis that the amount of degradable substrate is very small compared to the amount of biomass already present and hence the increase in the biomass concentration due to TBT degradation will be small. Kinetic constants were determined on the basis of Monod's kinetic model assuming negligible bacterial decay constant (b). The kinetic constants k (rate constant) and K_s were determined from the slope and intercepts of the least squares straight line fit of $-dt/ds$ vs. $1/s$ where s is the concentration of TBT and $-ds/dt$ is the rate of change of concentration.

Values of k and K_s for different concentrations are listed in Table 8.

TABLE 8. MONOD'S KINETIC CONSTANTS

8 day SRT				
Feed type	Inlet concentration TBT ($\mu\text{g/L}$)	K_s $\mu\text{gmol/L}$	k $\frac{\mu\text{gmol TBT}}{\text{mg bacteria} \cdot \text{hr}}$	r^2
Natural	50.0	1.34	0.33	0.92
	100.0	1.39	0.33	0.93
Synthetic	50.0	1.25	0.31	0.92
	100.0	1.32	0.32	0.85
18 day SRT				
Natural	50.0	1.34	0.32	0.76
	100.0	1.47	0.35	0.81
Synthetic	50.0	1.41	0.34	0.86
	100.0	1.35	0.33	0.95

K_s and k were obtained from a plot of $-dt/ds$ vs $1/s$ assuming constant bacterial concentration.

$$-\frac{dt}{ds} = \frac{K_s}{kX_0} \frac{1}{s} + \frac{1}{kX_0}$$

Data presented in Table 8 demonstrate that the biodegradation kinetic parameters for TBT were independent of SRT over the interval of 8-18 days. In addition, the parameter values for both natural and synthetic wastewater feeds were essentially the same.

BIOTIC STUDIES (ANAEROBIC SCREENING OF TBT)

Anaerobic treatment processes are widely used for biological stabilization of concentrated wastewater sludges. The objective of the screening study was to determine whether or not the anaerobic process was adversely affected by sludges containing sorbed TBT. A batch anaerobic bioassay technique based on the method developed by Owen (10) was used to determine the biochemical methane potential (BMP) and the anaerobic toxicity assay (ATA) for TBT.

The BMP assay was conducted in 250 mL reagent bottles and the ATA assay was conducted in 125 mL reagent bottles with rubber serum caps of appropriate sizes. Bottles were gassed at a flow rate of approximately 0.5 L/min with 30%

CO₂ and 70% N₂, then, stoppered and equilibrated at an incubation temperature 35°C prior to introducing samples, defined medium and inoculum. Defined medium was prepared using the recipe given in the Table 9 and stored at 4°C until needed.

TABLE 9. STOCK SOLUTIONS FOR DEFINED MEDIUM

Solution	Compound	Concentration g/L
S1	Sample	
S2	Resazurin	1.0
S3	(NH ₄) ₂ HPO ₄	26.7
S4	CaCl ₂ ·2H ₂ O	16.7
	NH ₄ Cl	26.6
	MgCl ₂ ·6H ₂ O	120.0
	KCl	86.7
	MnCl ₂ ·4H ₂ O	1.33
	CoCl ₂ ·6H ₂ O	2.0
	Na ₂ MoO ₄ ·2H ₂ O	0.17
	H ₃ BO ₃	0.38
	CuCl ₂ ·2H ₂ O	0.18
	ZnCl ₂	0.14
S5	FeCl ₃ ·4H ₂ O	370.0
S6	Na ₂ S·9H ₂ O	500.0
S7	Biotin	0.002
	Folic acid	0.002
	Pyridoxine hydrochloride	0.01
	Riboflavin	0.005
	Thiamin	0.005
	Nicotinic acid	0.005
	Pantothenic acid	0.005
	B ₁₂	0.0001
	p-aminobenzoic acid	0.005
	Thioctic acid	0.005

The defined medium contained nutrients and vitamins for mixed anaerobic cultures. Resazurin was added to detect oxygen contamination and sodium sulfide was added to provide a reducing environment. The final assay concentrations of nitrogen, phosphorus, and alkalinity were respectively: 12 mg/L as N, 19 mg/L as P, and 2500 mg/L as CaCO₃.

The defined medium was equilibrated at assay temperature, inoculated, and transferred into serum bottles. For BMP assay, inoculation was accomplished anaerobically by inserting a gas flushing needle into the neck of media flasks while adding 200 mL of seed organisms to 1800 mL of defined medium. A 20% by volume inoculum was used.

Figure 5 shows a schematic diagram of the procedure for anaerobic transfer of defined medium into serum bottles.

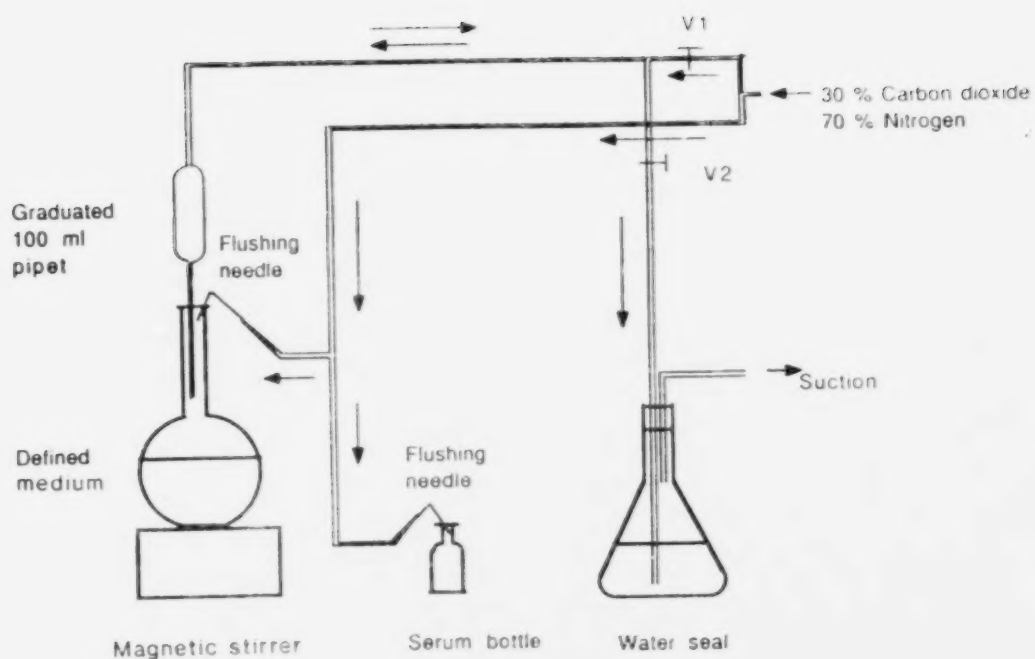


Figure 5. Schematic diagram of apparatus for anaerobic transfer of defined medium.

Care was taken to minimize the air to the anaerobic bottles. After the bottles were capped, they were zeroed with a syringe and incubated at 35°C.

In the BMP assay, seed blanks were prepared without addition of the organic substrate. Samples were anaerobically added to the bottles before the transfer of the inoculated defined medium and triplicates prepared for TBT at 10, 500, and 1000 µg/L.

In addition to the seed blanks, a spike of acetate and propionate was added to each bottle in the ATA assay. A control with only the spike was also prepared. Each bottle contained 75 mg acetate and 26.5 mg propionate.

Gas measurements for the first few days was critical for these studies. Gas produced was measured with a calibrated pressure transducer.

Figure 6 shows the cumulative methane gas production for ATA studies and as Figure 7 shows the cumulative gas production in BMP studies.

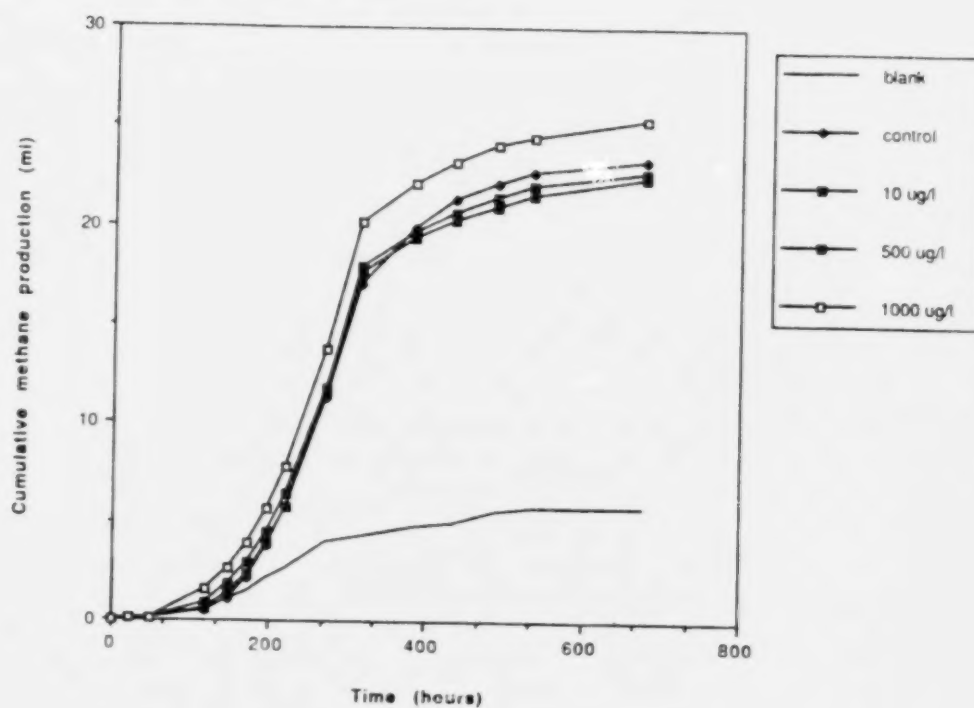


Figure 6. Cumulative methane production (ATA).

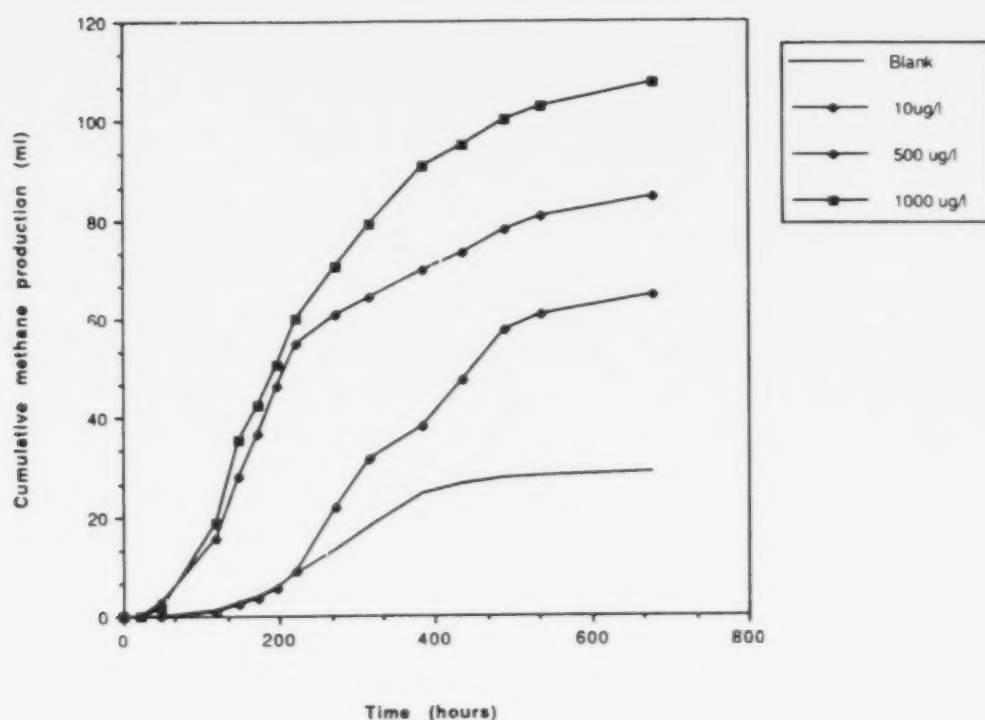


Figure 7. Cumulative methane production (BMP).

Cumulative methane production in the ATA Test was not affected by up to 1000 $\mu\text{g/L}$ of TBT as shown in Figure 6. Methane production in the BMP assay actually increased with increasing TBT concentration due to degradation of the additional alcohol solvent which was added to the samples with the higher doses of TBT. The magnitude of this effect is shown in Figure 7. Both ATA and BMP assays have shown that TBT is neither toxic nor inhibitory to anaerobic microbiota.

CONCLUSIONS

TBT and its degradation products were strongly sorbed to wastewater solids. Inhibition of normal biological treatment was not evident up to the solubility limit of TBT. Organotin compounds were biodegradable under acclimated conditions. Sorption on wastewater solids would be a dominant removal mechanism under unacclimated conditions. TBT sorbed on wastewater solids did not inhibit anaerobic processes. Fate of TBT and its degradation products in anaerobic treatment has not been determined.

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SUPERFUND TECHNICAL SUPPORT ACTIVITIES

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ABSTRACT

The Technical Support Branch of the Superfund Technology Demonstration Division of the Risk Reduction Engineering Laboratory, provides technical support to the EPA Regions through three programs: 1. Superfund Technical Assistance Response Team (START), 2. the Treatability Assistance Program and, 3. the Technology Support Project.

These programs offer engineering assistance on site-specific remediation problems through the use of RREL technology teams with expertise in the areas of incineration, materials handling, solidification/stabilization, extraction, chemical, biological, and aqueous treatment. The Branch also performs a number of technology transfer activities in order to provide engineering data and other information on Superfund site remediation to EPA Regions, and Program Offices, and to others. Technology transfer documents include treatment technology protocols and briefs, guidance documents on technical issues associated with RI/FS development, treatment technology vendors lists and treatment technology data bases. The Branch also coordinates Regional requests for RREL to perform in-house treatability studies.

"Guide for Conducting Treatability Studies under CERCLA"

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and

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Systematically conducted, well-documented treatability studies are an important component of the remedial investigation/feasibility study (RI/FS) process under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). These studies provide valuable, site-specific data necessary to aid in the selection of the remedy. This guide, which is being issued in interim final form, focuses on treatability studies conducted before the Record of Decision (ROD) has been signed; however, treatability studies may well continue into the remedial design/remedial action (RD/RA) phase.

The guide describes a three-tiered approach for conducting treatability studies that consists of: 1) laboratory screening, 2) bench-scale testing, and 3) pilot-scale testing. Depending on the information gathered during site characterization and technology screening and the data gaps that exist, treatability studies may begin with any tier (e.g., bench-scale testing) and may skip tiers that are not needed (e.g., laboratory screening followed by pilot-scale testing).

The guide also presents a stepwise approach or protocol for conducting treatability studies for determination of the effectiveness of a technology (or combination of technologies) in remediating a CERCLA site. The steps include: (1) establishing data quality objectives, (2) selecting a contracting mechanism, (3) issuing the Work Assignment, (4) preparing the Work Plan, (5) preparing the Sampling and Analysis Plan, (6) preparing the Health and Safety Plan, (7) conducting community relations activities, (8) complying with regulatory requirements, (9) executing the study, (10) analyzing and interpreting the data, (11) and reporting the results.

IMPLEMENTING A WASTE MINIMIZATION PROGRAM AT THE
A.W. BREIDENBACH ENVIRONMENTAL RESEARCH CENTER

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ABSTRACT

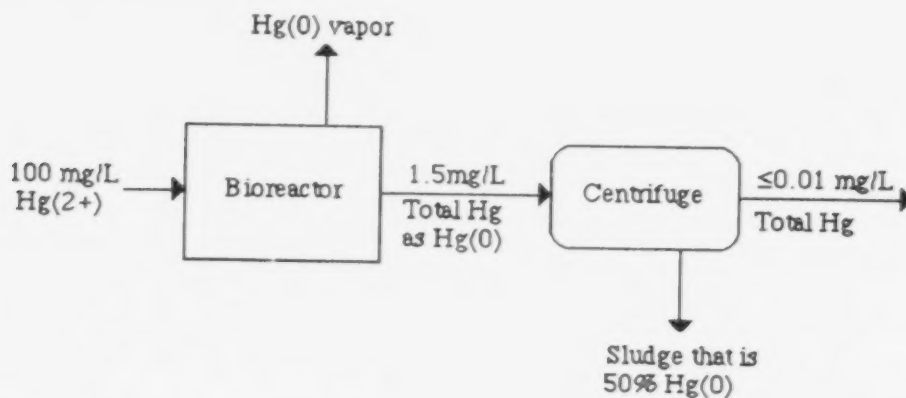
A permanent waste minimization program has been initiated at EPA's A.W. Breidenbach Environmental Research Center in Cincinnati, Ohio. The Waste Minimization Opportunity Assessment Manual (EPA/625/7-88/003) generic procedures were modified as needed to provide a basis for evaluation of wastes generated in the laboratories and offices at the Center. The waste minimization assessment team gathered information through a site visit and follow-up correspondence. Results of the assessment will be used to document waste minimization opportunities, strengthen the waste minimization program implementation plan, and identify research needs and potential demonstration projects for waste minimization at a laboratory and/or office facility.

BIOLOGICAL AND PHYSICO-CHEMICAL REMEDIATION OF A MERCURY CONTAMINATED HAZARDOUS WASTE

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ABSTRACT

Biological and physico-chemical removal of mercury from contaminated water and sediments involves enzymatic reduction of ionic mercury (Hg^{2+}) to the elemental form (Hg^0) and subsequent volatilization or precipitation. A continuous biological process for removing Hg^{2+} from water has been tested in laboratory scale. Greater than 99% of up to 100 mg/L influent Hg^{2+} can be removed using the process. A simplified schematic of the process is given below.



Hg^{2+} is reduced at a rate of 1.7 - 2.0 mg/L-h using an acclimated, mixed strain of mercury resistant bacteria improved over the years in our laboratory. Diluted whey permeate (10:1) is added in equal volumes with the Hg^{2+} contaminated water as an inexpensive nutrient source for the bacteria. Final disposition of most of the biologically reduced mercury is controlled by aeration rate, hydraulic retention time and Hg^{2+} loading rate. Volatilized Hg^0 is trapped by adsorption on activated carbon (AC) or chemically impregnated AC. Hg adsorbed on AC can be desorbed by heating. Desorbed vaporous Hg can be condensed for reuse.

STEAM STRIPPING AND BATCH DISTILLATION FOR REMOVAL AND/OR RECOVERY OF
VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

The Risk Reduction Engineering Laboratory of the U.S. Environmental Protection Agency Office of Research and Development is conducting treatment technology assessment for the RCRA listed hazardous wastes at its Cincinnati Test and Evaluation (T&E) Facility. As a part of this program, pilot-scale testing is being conducted to evaluate the performance of steam stripping and batch distillation for removal and/or recovery of volatile organic compounds. A 2-inch I.D. steam stripping column with packing equivalent to 20 theoretical plates has been selected for the testing. The batch distillation unit has a 125-gallon batch still and a 6-inch I.D. column with packing equivalent to 50 theoretical plates. At present, these units are in different stages of testing and shakedown. To date, steam stripping runs have been performed with toluene, isopropanol and 2-nitropropane. Different computer programs, for prediction of vapor-liquid equilibrium data and column design and/or evaluation have also been reviewed. Selected programs have been modified for use at the T&E Facility. A bench-scale unit is currently being set up to experimentally determine required vapor-liquid equilibrium data.

OZONE/ULTRAVIOLET LIGHT TREATMENT OF FERRI-CYANIDE COMPLEXES

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ABSTRACT

Recent concern over the quantity of total cyanide being disposed of in landfills and discharged to surface water has prompted the U.S. EPA Office of Solid Waste to begin investigating alternative treatment methods for electroplating wastewater. UV aided ozonation of ferri-cyanide complexes is one of the technologies currently being evaluated at the US EPA Test and Evaluation Facility in Cincinnati. Ferri-cyanide complex is a major cyanide source remaining after the destruction of free cyanide by alkaline chlorination. UV aided ozonation had been reported to have promise for treatment of ferri-cyanide complexes. In the current work the effects of different parameters, such as UV light intensity, temperature, ozone flow rate, and initial ferri-cyanide concentration, on the destruction rate of ferri-cyanide complex is being studied. This work will also include the determination of the effect of ozone activation by UV light in a separate chamber prior to ozone introduction into the reactor containing the ferri-cyanide solution.

THE USEPA/WRITE PROGRAM

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ABSTRACT

In 1989, the U.S. Environmental Protection Agency (USEPA) entered into cooperative agreements with six (6) states: California, Connecticut, Illinois, Minnesota, New Jersey, and Washington to participate in a new pollution prevention research program called Waste Reduction Innovative Technology Evaluation (WRITE). In this three (3) year program, the states work with industry to demonstrate and evaluate source reduction and recycling technologies to reduce or eliminate waste. Technology evaluations will include both engineering effectiveness and cost analysis. This presentation will focus on two (2) of these WRITE programs: Illinois and New Jersey.

Illinois

In June of 1989, the Illinois Hazardous Waste Research and Information Center (HWRIC) and the USEPA began a three (3) year program. Some projects under consideration include substituting water-based and nontoxic liquid cleaners in flexographic printing, soybean-based inks in off-set printing, closed loop recycling and substituting zinc hydroxide for zinc cyanide in an electroplating process and other projects. Discussion will focus on the approach, methods, and technologies.

New Jersey

In August of 1989, the New Jersey Department of Environmental Protection (NJDEP) and USEPA began this three (3) year project. Some of the technologies being considered are: an electroplating wastewater recycling system, substitution of a colloidal compound cleaner for degreasing operations, and other projects. Discussion of the project will include project objectives and approach, obstacles encountered and technologies under consideration.

AMERICAN INSTITUTE FOR POLLUTION PREVENTION

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ABSTRACT

The Environmental Protection Agency, jointly with the University of Cincinnati, formed the American Institute for Pollution Prevention (AIPP) in June 1989. The Institute's primary goal is to generate broad support from the public and private sectors and assist EPA in achieving the widespread and expeditious adoption of pollution prevention concepts.

The EPA approach to pollution prevention is somewhat unique among all other EPA environmental protection efforts in that it is not a regulatory-based, adversarial type program but rather must achieve success by relying on information transfer and persuasion with respect to both the motivation of pollution generators to incorporate pollution prevention practices and how, from a technical viewpoint, pollution prevention can be achieved.

AIPP members have been nominated by their respective professional societies or trade associations and have individually demonstrated numerous accomplishments in the field of pollution prevention. They have all agreed to serve voluntarily because of their continuing interest in environmental protection. The AIPP has formed four Councils to address its goals in the areas of economics, education, implementation and technology.

U.S. EPA INCINERATION RESEARCH FACILITY UPDATE

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ABSTRACT

In the last few years, the EPA Incineration Research Facility (IRF, formerly CRF) in Jefferson, Arkansas has conducted incineration tests at an accelerated pace to meet the data needs of the Agency. In FY'89, its physical plant underwent a major expansion. A new building, completed in July 1989, increased the enclosed space to 15200 square feet and provided a facility more consistent with the increasing level of activities.

Concurrent with building construction, the rotary kiln incinerator system (RKS) was reconfigured to improve several aspects of its operation. These included implementing more ideal sampling ports at the afterburner exit; relocating the scrubber system to allow easy connection of alternate air pollution control systems (APCS); replacing the secondary APCS by one of improved design; and making arrangements for an automatic control system for the entire RKS.

Ongoing research at the IRF focused on providing support to Regional Office remediation efforts by conducting treatability tests. Two test series were completed in FY'89. One looked at the applicability of incineration in decontaminating arsenic-contaminated soil at a Region 1 Superfund site. The other studied the treatability of the contaminated-soils at two Superfund sites in Region 9.

Another series of parametric tests continued the study on the distribution of toxic trace metals in incinerator systems. A previous series was conducted with a venturi/packed column scrubber for air pollution control. The recent series was conducted with an ionizing wet scrubber.

Planned test programs include POHC incinerability ranking evaluation; a listed waste BDAT evaluation; continued trace metal distribution studies with alternate APCDs; further testing to support Regional remediation effort; and third party testing as provided for by the Federal Technology Transfer Act.

DEVELOPMENT AND DEMONSTRATION OF A PILOT-SCALE DEBRIS WASHING SYSTEM

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ABSTRACT

A large number of hazardous waste sites in the United States are littered with metallic, masonry, and other solid debris which may be contaminated with hazardous chemicals [e.g., polychlorinated biphenyls (PCBs), pesticides, lead, or other metals] and in some cases clean-up standards have been established ($10 \mu\text{g PCBs}/100 \text{ cm}^2$ for surfaces to which personnel may be frequently exposed). Although the majority of debris at Superfund sites does not possess the potential for reuse, the debris could, following decontamination, either be returned to the site as "clean fill" in lieu of transporting the debris offsite to a hazardous waste landfill or, in the case of metallic debris, be sold to a metal smelter.

During previous phases of this project we have developed a technology for performing on-site decontamination of debris. Both bench-scale and pilot-scale versions of a Debris Washing System (DWS) have been designed and constructed. The DWS utilizes an aqueous solution which is applied to the debris during a high pressure spray cycle followed by a turbulent wash cycle. The aqueous cleaning solution is recovered and reconditioned for use concurrently with the actual debris cleaning process; therefore the quantity of process water utilized to clean the debris is minimized.

In this paper, we present the results obtained during a field demonstration of the DWS. Data will be presented which are indicative of the effectiveness of the system for removing PCBs from the surfaces of metallic debris, as well as the efficiency of the closed-loop solution reconditioning system which is built into the DWS. The performance of the DWS under adverse (sub-freezing) temperature at a hazardous waste site located in Hopkinsville, Kentucky will also be discussed.

ENGINEERING HANDBOOK FOR HAZARDOUS WASTE INCINERATION

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One of the most difficult, and time-demanding, tasks for a permit writer is to evaluate and interpret incinerator designs and to determine whether the construction and testing of a hazardous waste incinerator will cause an unreasonable impact on health and the environment. In addition, individuals must understand the fundamentals of incinerator construction and operation to design trial burns and to evaluate the results. This paper describes the revised Engineering Handbook for Hazardous Waste Incineration, a document due to be published in late 1990 which will provide guidance on the basic principles, concepts and designs of hazardous waste incinerators. The Engineering Handbook will also give methods that can be used to estimate the performance of the incinerator and its ancillary equipment.

The Engineering Handbook is an extensive revision and update of SW-889, a document by the same name which was published in 1981. It is a compilation of information from the open literature describing current techniques and equipment used for hazardous waste incineration. The document is not intended to be a detailed design handbook, rather it is intended as a reference for those individuals who are associated with the regulatory aspects of the subject. It is specifically aimed at permit writers and regulators who are generally unfamiliar with the field and need a central source of basic information. As such, its main emphasis is on the evaluation of equipment and their designs to assess how well new incinerators, whose designs are being evaluated prior to construction, are likely to achieve their function in a safe and environmentally sound manner. The Handbook also contains fundamental thermodynamic and kinetic information and techniques that can be used to evaluate, design and operate a facility.

This work is being conducted under EPA contract 68-C8-0011, WA 1-30 to the Eastern Research Group, Inc. LVW Associates, Inc., the Environmental Research Division of Acurex Corporation and John Richards, are participating as consultants and subcontractors. The work is being performed under the joint guidance and sponsorship of the Office of Solid Waste and the Office of Research and Development of the U.S. Environmental Protection Agency.

AN ASSESSMENT OF THE CURRENT STATE OF THE ART OF
BIO/PHOTODEGRADABLE PLASTICS

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ABSTRACT

The focus of this project has been to assist EPA in developing parameters to support Federal regulation of the disposal of consumer-use plastic products such as polyethylene, polyvinyl chloride (PVC), and polystyrene. Although plastics recycling is increasing, major concern still exists regarding the fate of these products and their ecological effects in the soil and the marine environment. Objective methods are needed to define degradation, deterioration, and decomposition and to judge the relevance and value of engineering tests.

The authors recommend that 6-pack carrier rings be manufactured from photodegradable materials, and they conclude that insufficient research has been conducted to evaluate engineering tests. The project also includes a review of State and local regulation of plastics.

FIELD TESTS OF HYDRAULIC FRACTURING TO INCREASE FLUID FLOW IN SOILS

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Fluid flow in the subsurface is a basic requirement of many methods of in-situ remediation, including pump and treat, soil flushing, vapor extraction, bio-remediation, and steam stripping. Hydraulic fracturing is a method of increasing fluid flow to improve the effectiveness of those in-situ methods, especially in areas where flow is limited by material of low permeability. Basically, hydraulic fracturing involves injecting fluid into a well until pressures exceed a critical value and fracturing begins. Sand is then pumped into the fracture to hold it open and provide a high permeability channelway. The process was developed more than fifty years ago to increase the yields of oil wells. Last year at the Symposium we reported results from our first field test where we used oil-field equipment to show that it was possible to create hydraulic fractures at shallow depths in soil-conditions typical of many contaminated sites.

Shortcomings of the 1988 test led us to redesign equipment and methods of hydraulic fracturing at shallow depths. The new method, which employs equipment similar to that used for grouting, was field tested in June 1989 with the creation of 23 fractures at two sites in Cincinnati, Ohio. Both sites are underlain by overconsolidated, silty-clay till. Nineteen of the fractures were excavated to examine their size, thickness and orientation. The excavated fractures all contained sand and they reached a maximum thickness of one inch and a maximum length of 28 feet. As many as four flat-lying fractures, stacked one on top of another at spacings as close as 6 inches, were created from the same borehole. Venting of the fractures to the ground surface was reduced compared with results from 1988. Steady-state rates of inflow into boreholes intersecting hydraulic fractures were 3.2 and 9.1 greater than steady rates into boreholes in unfractured till, according to results of tests conducted using a constant-head permeameter.

BARRIER EQUIVALENCY OF LINER AND CAP MATERIALS

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ABSTRACT

The objective of this project is to investigate materials that might be used as hydraulic barriers in liners or covers to replace or augment a low-permeability, compacted soil liner. In the first year of investigation, potentially equivalent barrier materials were identified, and available data for the materials were collected, tabulated, and analyzed. Additional data that would be needed to determine the equivalency of the barriers were identified. In the next year of study, tests will be performed to aid in determining the equivalency of the materials to a low-permeability, compacted soil liner.

The materials that were investigated included blended soils, amended soils, manufactured blankets of clay, waste materials, concrete, sprayed-on materials, and manufactured membrane/clay composites. The materials fell into two categories: 1) materials that would have to be custom-designed and evaluated for each project, and 2) manufactured, "off-the-shelf" materials, the properties of which would not have to be repeatedly studied. Future emphasis will be placed on the second category of materials. The greatest amount of data and experience in the field was found for thin blankets of bentonite attached either to geotextiles or membranes. These materials show promise as equivalent barriers, but more data are needed to define characteristics of seam overlaps, puncture resistance, resistance to desiccation and frost action, and similar performance parameters.

ABSTRACT

An Upcoming S.I.T.E. Demonstration:
AWD Technologies, Inc., "AquaDetox/SVE System"

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As part of the Agency's Superfund Innovative Technology Evaluation (SITE) Program, a demonstration of AWD Technologies "AquaDetox/SVE System" will be conducted during the summer of 1990. The process is an automated system which combines a vacuum steam stripping tower (the AquaDetox unit) with a soil vapor extraction (SVE) unit into a closed-loop system. According to the developer, the system is capable of removing more than 90 of the 110 volatile compounds listed in CFR 40, July 1, 1989, by the U.S. EPA. Within the AquaDetox system, contaminated groundwater enters the top of a stripping tower that operates under a moderate vacuum. Steam is injected from the bottom. Contaminants are stripped from the water, condensed, and collected for later recycling. The SVE System removes contaminated soil-gases from the vadose zone through a network of extraction wells. These soil-gases are then exhausted to a series of granular activated carbon beds for hydrocarbon removal. The cleaned gases are then reinjected into the ground. The ability of this system to clean contaminated groundwater and soil-gases in a closed-loop system eliminates the possibility of air emissions, and thus the need to obtain air quality permits.

The demonstration will occur as a part of an ongoing remediation at the Lockheed Aeronautical Systems facility in Burbank, Ca. (part of the San Fernando Superfund Site). Among the innovative design features is the addition of an automatic regeneration system for the granular activated carbon beds. Steam is used from the AquaDetox unit to strip the hydrocarbons from the beds. This vapor is sent back to the AquaDetox unit, condensed, and is also collected for recycling. One of the points which the SITE Program will investigate is the developer's claim that the system enjoys a cost advantage over dual-stage stripping systems.

GUIDANCE ON METALS AND PIC EMISSION CONTROLS FROM HAZARDOUS
WASTE INCINERATION

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ABSTRACT

The U.S. Environmental Protection Agency (EPA) is currently working on regulations to control emissions of heavy metals and Products of Incomplete Combustion (PICs) when hazardous waste is incinerated in incinerators, boilers or industrial furnaces like cement kilns. The EPA has also published guidance manuals for use by the permit writers in the Regions and the States so that they can implement the proposed controls in the interim, until the final rules are promulgated, using omnibus authority provided to the permit writers under RCRA section 3005(c)(3). The methodology to control carcinogenic metals (arsenic, beryllium, cadmium and chromium) emissions has been provided such that the incremental lifetime risk to the maximum exposed individual (MEI) does not exceed 10^{-5} . The control for PIC emissions is provided by using Carbon Monoxide (CO) and Total Hydrocarbon (THC) emissions from the stacks as surrogates. The CO must be monitored continuously and must not exceed 100 parts per million by volume (ppmv) corrected to 7% oxygen and on a dry basis. In cases where the CO exceeds the above level, the compliance must be demonstrated by monitoring THC emissions which should not exceed 20 ppmv. Also, the THC should be monitored continuously in addition to CO during the life of the permit in those cases.

The regulatory proposal for hazardous waste incineration in boilers and industrial furnaces was published in the Federal Register (54 FR 43718) on October 26, 1989 and for incinerators in the Federal Register (55 FR 17862) on April 27, 1990. The final promulgation is expected in 1991 for both the proposals.

Reduction of Transient Puffs from a Rotary Kiln Incinerator:
The Role of the Secondary Combustion Chamber

by

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ABSTRACT

Experiments on a 73 kW (250,000 Btu/hr) rotary kiln incinerator simulator equipped with a 58.4 kW (200,000) Btu/hr afterburner/control temperature tower were performed to examine the effect of the secondary combustion chamber on reducing transient puffs generated during the batch charging of surrogate solid waste. In this preliminary set of tests, the effects of temperature, oxygen and residence time were examined in the absence of flame contact and turbulent mixing. A first generation deterministic model is being developed to examine the response of the secondary combustion chamber to a transient input. Preliminary data indicate that not only does the secondary chamber provide a reduction in the absolute magnitude of a puff, but also considerably alters the composition of the puff, with respect to both chemical species and biological activity.

THE USE OF ELECTROKINETICS
FOR HAZARDOUS WASTE SITE REMEDIATION

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ABSTRACT

This study was performed to assess the state-of-the-art of electrokinetically-enhanced contaminant removal in soils. Prior research efforts, both laboratory and field, have demonstrated that electroosmosis has the potential to be effective in facilitating the removal of certain types of hazardous wastes. Particularly encouraging results have been achieved with inorganics in fine-grained soils where more traditional removal alternatives such as pump and treat are less effective.

Although the results of various studies suggest that electrokinetics is a promising technology, further testing is needed at both the laboratory and field levels to fully develop this technology for site remediation. A conceptual test program is presented based on best available data which incorporates system design and operating parameters used in previous applications of this technology.

GROUND PENETRATING RADAR EQUIPPED FIELD ROBOTIC VEHICLE
FOR SURVEYING CERCLA SITES

by:

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ABSTRACT

For years, robotics and automation have increased productivity in manufacturing industries through standardization and repeatability. Core robotic technologies have now progressed to the point that robots are moving into the field and offering the same benefits. One such implementation is subsurface mapping of waste sites – the process of spatially correlating non-invasive measurements in order to graphically represent the geometry of buried structures. Through a cooperative agreement with the US EPA, the Field Robotics Center is developing a subsurface mapping system based on a mobile robot that deploys ground penetrating radar (GPR) transducers.

This prototype Site Investigation Robot (SIR) maintains knowledge of its location on site and carries a scanning mechanism that provides the local positional accuracy necessary for GPR imaging. GPR data are digitized and stored in memory for subsequent digital filtering, specialized geophysical processing and image enhancement. These processes transform the radar data into a subsurface map which is displayed on a computer graphics terminal and stored in the site database. While we have demonstrated these techniques for two dimensional GPR images, the focus of our current research is development of processing techniques that exploit the three-dimensional nature of GPR and create 3-D subsurface maps.

DETOXIFICATION OF RELEASED VAPORS/PARTICULATES BY ENTRAPMENT
IN CHEMICALLY ACTIVE FOAMS

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ABSTRACT

In the wake of the Bhopal disaster, there has been increasing public and governmental concern over the possibility of toxic gas and vapor releases from chemical plants. Title III of SARA, "Superfund Reauthorization and Amendment Act of 1986", specifically addresses emergency preparedness for such releases. Industry is under intense pressure to provide additional safeguards to prevent "gas" clouds from threatening populated areas.

Many ways to prevent releases are already in use by industry ranging from safety-conscious plant design, through safety alarms and interlocks, to backup devices such as scrubbers and flares. However, once a gas or vapor leak occurs, the options for its control are few.

Under study is the use of "foam scrubbing," a novel option for controlling emergency releases of airborne toxics. In this approach, foam is generated with conventional equipment using the contaminated air. The foaming solution contains neutralizing agents and may require a special surfactant system for compatibility. With the airborne materials encapsulated in the foam, a large interior liquid surface area is available for gas, vapor, aerosol, or particulate sorption. Neutralization agents present in the bubble walls can then react with the entrapped toxic gas or vapor to render it innocuous. The foam collapses to yield a processable liquid.

This proposed technology has potential applications to emergency control; among these are fixed installations in plants and portable units for field use by emergency response teams.

ASSESSMENT OF MATERIALS HANDLING TECHNOLOGIES

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ABSTRACT

A typical Superfund or other hazardous waste site contains hazardous chemicals which are frequently intermingled with remnants of razed structures as well as contaminated soil, gravel, concrete, and metallic debris. Specialized materials handling and classifying technologies are needed to deal with the large quantities of these various types of contaminated materials present at the site prior to, or in conjunction with decontamination and disposal operations. The objective of this study is to summarize the types of debris, material, and contaminants found at Superfund and other hazardous waste sites in EPA Region V and the materials handling equipment and general procedures that have been implemented to perform site restoration and cleanup.

This paper provides information on state-of-the-art materials handling equipment and procedures that would be useful for addressing difficult, site-specific, materials handling problems. The capabilities, performance, applicability for hazardous waste site work, and costs for a variety of materials handling techniques will be discussed. Case studies for sites within EPA Region V will be presented which include detailed information concerning debris, material, contaminants found on site, and the specific materials handling needs and problems encountered. In addition, the materials handling technologies currently used in the United Kingdom and West Germany will be briefly summarized.

METAL TREATMENT BY ADSORPTIVE FILTRATION

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ABSTRACT

Treatment of solutions containing toxic metals at Superfund sites is complicated by the wide range of concentrations which may be present and the complexity of the matrix. Although highly concentrated metals may be treatable by conventional precipitation processes, these processes may not meet the stringent effluent discharge requirements. Also, metals are often present in relatively low, but still unacceptable concentrations in the effluent from treatment processes for removal of organic contaminants.

The process being tested in this project is one which combines an efficient sand filter with an adsorption process capable of lowering metal concentrations well below levels achievable by precipitation alone. The process uses a conventional sand filter in which the sand is first coated with iron oxide. The iron oxide surface has a strong pH-reversible affinity for the metals. The fact that the oxide is physically attached to sand grains rather than a suspended material makes it much easier to work with, and allows the filtration of particulate metal contaminants to proceed simultaneously with adsorption from the soluble phase. Finally, the process is applicable to anionic metals such as chromate, selenite, and arsenate, which are difficult to precipitate efficiently.